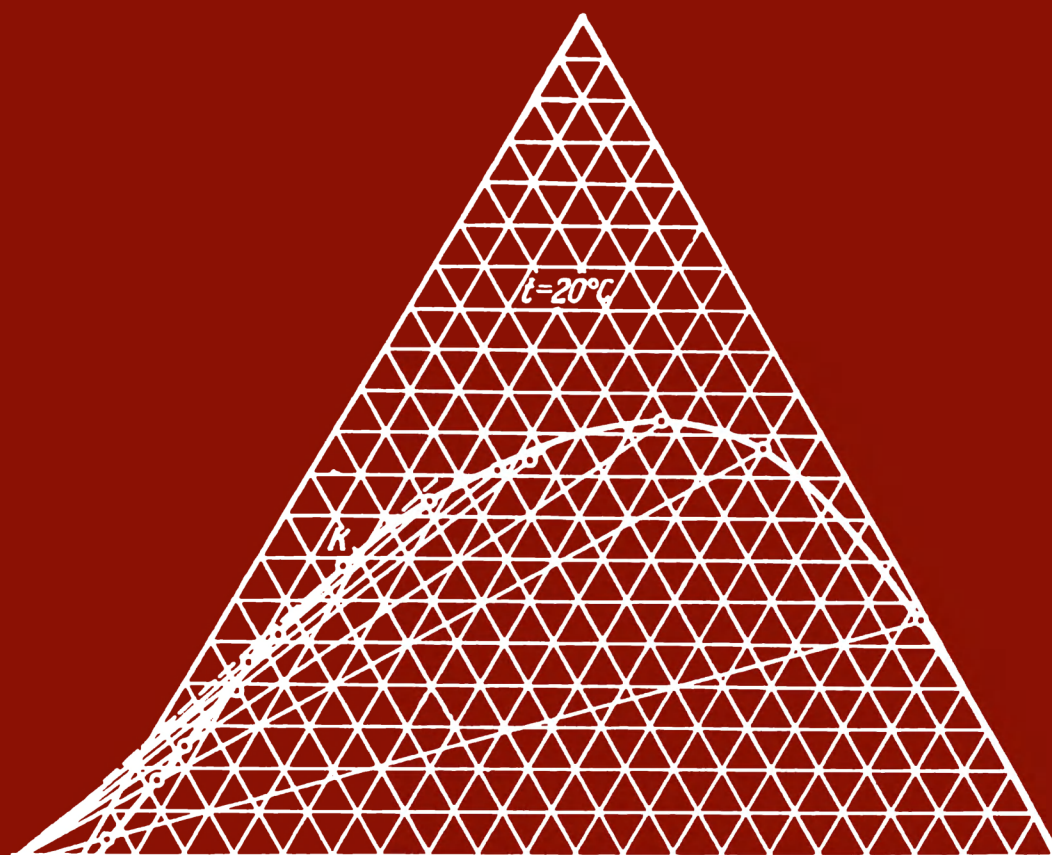


EXAMPLES AND PROBLEMS IN CHEMICAL THERMODYNAMICS

M. Kh. Karapetyants



MIR PUBLISHERS

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М. Х. Карапетьянц

ПРИМЕРЫ И ЗАДАЧИ ПО ХИМИЧЕСКОЙ ТЕРМОДИНАМИКЕ

ИЗДАТЕЛЬСТВО «ХИМИЯ» МОСКВА

M. Kh. Karapetyants

EXAMPLES
and
PROBLEMS
in
CHEMICAL
THERMODYNAMICS

Translated from the Russian

by

G. Leib

MIR PUBLISHERS

First published 1976
Revised from the 1974 Russian edition

На английском языке

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Preface

The present textbook is a study aid to the course in chemical thermodynamics. The examples and problems contained in it cover the most essential and characteristic sections of the course, which should assist students to master the elementary methods of both general thermodynamic calculations and special ones connected with separate processes of chemical technology.

The topics of the examples and problems mainly reflect questions of the technology of inorganic production processes and the chemical processing and refining of fuel. In this connection the main attention has been devoted to gaseous systems.

Each chapter of the book begins with a brief theoretical introduction containing the equations and formulas needed for calculations. This is followed by examples with detailed solutions and problems. The examples contain all the data necessary for calculations and can be used for independent solution. In compiling the book, the author tried to avoid identical examples and problems (using the same formulas and quantities, but describing different objects).

For a greater approximation to practical calculations, the book acquaints students with approximate methods of computations, graphical methods of calculations and with some semi-empirical and empirical laws. The results of the calculations, when possible, are compared with experimental data or with calculations by other methods, which makes it possible to assess the accuracy of different methods and the limits of their application.

A considerable part of the examples and problems have been drawn up according to the published works of Soviet investigators. The experimental data are also taken from reference books and monographs. Some problems have been taken from different textbooks.

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List of Symbols*

<i>A</i>	coefficient; factor; Helmholtz energy	<i>k</i>	Boltzmann constant; Henry's coefficient; number of identical substituents
<i>a</i>	activity; constant; number of bonds permitting free rotation	<i>M</i>	molecular weight (mass)
<i>B</i>	coefficient	<i>m</i>	molality; number of atoms; number of moles per mole
<i>b</i>	constant	<i>N</i>	number of atoms
<i>C</i>	coefficient; constant; heat capacity	<i>N_A</i>	Avogadro constant
<i>c</i>	coefficient; concentration; velocity of light	<i>n</i>	number of bonds, moles, atoms in a molecule; valence
<i>d</i>	coefficient	<i>P</i>	parachor
<i>E</i>	Einstein function; electromotive force (e.m.f.)	<i>p</i>	pressure
<i>e</i>	base of natural logarithms	<i>Q</i>	heat
<i>F</i>	Faraday constant	<i>q</i>	number of valence bonds in a molecule; solubility
<i>f</i>	fugacity; function	<i>R</i>	universal gas constant, equal to $1.987\,19 \pm 0.00013$ cal/K; in this book the value of <i>R</i> is taken equal to 1.987 cal/K = 82.06 cm ³ ·atm/K = 8314.4 J/K
<i>G</i>	Gibbs energy	<i>S</i>	entropy
<i>g</i>	acceleration of gravity; statistical weight	<i>T</i>	absolute temperature
<i>H</i>	enthalpy	<i>t</i>	temperature, °C
<i>h</i>	Planck constant	<i>U</i>	internal energy
<i>I</i>	integration constant; ionic strength of solution; moment of inertia	<i>V</i>	volume
<i>i</i>	conditional chemical constant	<i>v</i>	specific volume
<i>j</i>	true chemical constant	<i>W</i>	work
<i>K</i>	cryoscopic constant; equilibrium constant; partition coefficient		

* In the English translation of this book the recommendations contained in the Manual of Symbols and Terminology for Physicochemical Quantities and Units adopted by the IUPAC Council at Cortina d'Ampezzo, Italy, on July 7, 1969 (see Pure and Applied Chemistry, Vol. 21, No. 1, 1970) have been used wherever possible.—*Translator's note.*

w	valence; weight of component	*	substance belonging to a system in the idealized state corresponding to an infinitely small pressure
x	correction; dryness fraction; mole fraction	c	crystalline state
y	degree of oxidation	g	gaseous state
Z	atomic number; compression factor	lq	liquid state
z	charge of ion; valence	Subscripts	
α	constant; cubic expansion coefficient	aq	infinitely dilute aqueous solution
γ	activity coefficient; characteristic frequency; isochoric pressure coefficient; ratio of heat capacities (C_p/C_v)	av	average
Δ	heat correction; increment	b	boiling
δ	increment	comb	combustion
ε	energy of bond breaking; energy of molecule at i -th level	cr	critical
Θ	characteristic temperature	eq	equilibrium
κ	isothermal compressibility	eut	eutectic
μ	Joule-Thomson coefficient	form	formation
ν	frequency; stoichiometric coefficient	fus	fusion
π	reduced pressure	id	ideal
ρ	density	in	initial
Σ	sum	inv	inversion
σ	symmetry number	mix	mixture
τ	reduced temperature	n.b.p.	normal boiling point
Superscripts (relating, as a rule, to a phase)		n.m.p.	normal melting point
$^{\circ}$	pure substance or one in the standard state	osc	oscillation
		ph.tr	phase transition
		pr	product
		r	reactant
		s	solidification (freezing)
		sat	saturated
		subl	sublimation
		tr	transition
		vap	vaporization
		0	property at $T=0$
		1	solvent; initial state
		2	solute; final state

The Greek letter Δ in front of a thermodynamic function (for example ΔG) means that the change (final minus initial) is referred to.

The subscripts p , T and V indicate that the quantity they relate to is at constant pressure, temperature or volume, respectively (for example C_p is the heat capacity at constant pressure).

A numerical subscript indicates the absolute temperature (decimal fractions are usually discarded) if it is not preceded by the symbol of another quantity.

In mastering sciences examples are more useful than rules.

ISAAC NEWTON

Chapter One

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics follows from *Lomonosov's law* and states the principle of conservation and conversion of energy as applied to thermodynamic processes.

Consider the heat Q supplied to a system and the work W done by the system to be positive. Hence for an infinitely small change in the state of the system performing a *non-cyclic* process we have

$$\delta Q = dU + \delta W = dU + p dV + \delta W' \quad (1.1)$$

where dU = change in the internal energy
 $\delta W' = \delta W - p dV$ = elementary work for overcoming all the forces except the external pressure (as a rule $\delta W' = 0$).

Introducing the function H (the *enthalpy*), determined by the equation

$$H \equiv U + pV \quad (1.2)$$

we get

$$\delta Q = dH - V dp + \delta W' \quad (1.3)$$

For a finite *cyclic* process

$$Q = W \quad (1.4)$$

In all the equations Q , W , U and H are expressed in the same units (customarily in calories or joules).

Examples

1. Show that for a finite change in the state of 1 mole of an ideal gas whose internal energy depends only on the temperature, and the relationship between the pressure, volume and temperature is expressed by the *Mendeleev-Clapeyron equation*

$$pV = RT$$

Eq. (1.1) acquires the form

$$\delta Q = C_V dT + RT d \ln V$$

Solution. Since the internal energy of an ideal gas depends only on the temperature, then

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT$$

Inserting this value of dU into Eq. (1.1) and assuming that

$$p = \frac{RT}{V} \quad \text{and} \quad \delta W' = 0$$

we get

$$\delta Q = C_V dT + RT d \ln V$$

2. 100 Grammes of nitrogen are at a temperature of $t=0^\circ\text{C}$ and a pressure of $p=1$ atm. Using the equation derived in solving Example 1, find Q , ΔU and W for:

- (1) isothermal expansion to a volume of 200 dm³;
- (2) an isochoric increase of the pressure to 1.5 atm;
- (3) isobaric expansion to a double volume.

Assume that $C_p=6.960$ cal/mol·K and $C_p-C_V=R$.

Solution. 1. For an isothermal process the above equation acquires the form

$$Q = nRT \ln \frac{V_2}{V_1}$$

where n is the number of moles of nitrogen (in our example $n=100/28.02$).

The quantity V_1 is found by the Mendeleev-Clapeyron equation

$$V_1 = \frac{nRT}{p_1} = \frac{(100/28.02) \times 82.06 \times 273.2}{1} = 80\,010 \text{ cm}^3 = 80.01 \text{ dm}^3$$

Consequently

$$Q = \frac{100}{28.02} \times 1.987 \times 273.2 \times 2.303 \log \frac{200}{80.01} = 1775 \text{ cal}$$

$$\Delta U = 0 \quad \text{and} \quad W = 1775 \text{ cal}$$

2. For an isochoric process

$$\delta Q = C_V dT$$

For n moles, provided that $C_V=\text{const}$, we have

$$Q = nC_V(T_2 - T_1)$$

We determine the temperature after compression according to the Mendeleev-Clapeyron equation. Since at $V=\text{const}$

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}$$

then

$$T_2 = 273.2 \times \frac{1.5}{1} = 409.8 \text{ K}$$

Therefore

$$Q = \frac{100}{28.02} \times (6.960 - 1.987) (409.8 - 273.2) = 2424 \text{ cal}$$

$$\Delta U = 2424 \text{ cal} \quad \text{and} \quad W = 0$$

3. For an isobaric process

$$\delta Q = C_p dT$$

For n moles provided that $C_p = \text{const}$, we have

$$Q = nC_p(T_2 - T_1)$$

The temperature after expansion is determined according to the Mendeleev-Clapeyron equation. Since at $p = \text{const}$

$$\frac{T_2}{T_1} = \frac{V_2}{V_1}$$

then

$$T_2 = T_1 \frac{V_2}{V_1} = 273.2 \times 2 = 546.4 \text{ K}$$

Consequently

$$Q = \frac{100}{28.02} \times 6.960 (546.4 - 273.2) = 6786 \text{ cal}$$

$$\begin{aligned} W &= np(V_2 - V_1) = nR(T_2 - T_1) = \\ &= \frac{100}{28.02} \times 1.987 (546.4 - 273.2) = 1937 \text{ cal} \end{aligned}$$

and

$$\Delta U = Q - W = 4849 \text{ cal}$$

3. A vessel with a capacity of 1 dm³ (one litre) contains saturated steam at a pressure of 30 kgf/cm². Its specific volume equals 0.06802 m³/kg. What amount of heat must be removed to achieve condensation of half of the steam in the vessel? Neglect the volume of the liquid.

Solution. The vessel contains

$$\frac{0.001}{0.06802} = 0.0147 \text{ kg of steam}$$

Neglecting the volume of the liquid in accordance with the initial conditions, we find that after condensation there will remain

$$0.5 \times 0.0147 = 0.00735 \text{ kg of steam}$$

and its specific volume will equal

$$\frac{0.001}{0.00735} = 0.1361 \text{ m}^3/\text{kg}$$

A pressure of the saturated steam equal to 14.8 kgf/cm² (found by interpolation from reference data) corresponds to this specific volume.

Since condensation proceeds at constant volume, the removed heat is equal to the reduction in the internal energy. In accordance with Eq. (1.2) and with the fact that 1 kcal is equivalent to 426.9 kgf·cm, we find, assuming $H_1=669.7$ kcal (from a reference book)

$$U_1 = H_1 - p_1 V_1 = 669.7 - \frac{30 \times 10^4 \times 0.06802}{426.9} = 621.9 \text{ kcal/kg}$$

Since

$$U_2 = U^{lq} + 0.5 \Delta U_{vap}$$

then, assuming that $U^{lq} \approx H^{lq} = 199.9$ kcal/kg (found by interpolation from reference data), we get

$$U_2 = H^{lq} + 0.5 (U^c - U^{lq}) = 199.9 + 0.5 (621.9 - 199.9) = 410.9 \text{ kcal/kg}$$

Consequently

$$-\Delta U = 621.9 - 410.9 = 211.0 \text{ kcal/kg}$$

i.e. it is necessary to remove

$$0.0147 \times 211.0 = 3.102 \text{ kcal}$$

4. What quantity of heat has to be removed in compressing 1 kg of steam from $p_1=10$ to $p_2=50$ kgf/cm² to ensure an isothermal nature of the process if $t=350^\circ\text{C}$? Use the following data for the calculations:

p , kgf/cm ²	10	20	30	40	50
v , m ³ /kg	0.2879	0.1412	0.092 39	0.067 82	0.053 10
Hg , kcal/kg	753.6				732.0

Solution. In accordance with Eq. (1.3) we have

$$Q = \Delta H - \int_{p_1}^{p_2} v dp$$

Therefore

$$Q = (732.0 - 753.6) - \int_{10}^{50} v dp$$

We determine the integral graphically (Fig. 1) as the area bounded by the curve $v=\varphi(p)$, the vertical lines $p_1=10$ and $p_2=50$ kgf/cm² and the axis of abscissas. With a view to the scale of the chart (the shaded area contains 180 squares with sides of 0.01 m³/kg and 2.5 kgf/cm²)

we find that

$$\int_{10}^{50} v dp = 180 \times 0.01 \times 2.5 = \frac{4.5 \times 10^6 \text{ atm} \cdot \text{cm}^3}{1.033 \text{ kg}} = \frac{4.35 \times 10^6}{41.293^* \times 1000} = -105.4 \text{ kcal/kg}$$

Hence

$$Q = -21.6 - 105.4 = -127 \text{ kcal/kg}$$

5. The first law of thermodynamics can be written as follows:

$$\delta Q = X dx + Y dy$$

where x and y = thermodynamic parameters

X and Y = so-called *caloric coefficients*.

Six caloric coefficients are possible with three thermodynamic parameters (p , V and T). Find these quantities and indicate their physical meaning.

Solution. The total number of possible equations is three:

$$\delta Q = X_p dT + Y_T dp$$

$$\delta Q = X_V dp + Y_p dV$$

$$\delta Q = X_T dV + Y_V dT$$

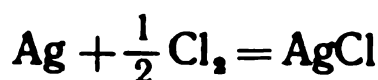
where X_p and Y_V = isobaric and isochoric (isometric) heat capacities

X_T and Y_T = "latent" heats of isothermal expansion and compression

X_V = coefficient characterizing the use of heat for an isochoric change of the pressure; $X_V = (\delta Q / \partial p)_V$

Y_p = coefficient characterizing the use of heat for isobaric expansion; $Y_p = (\delta Q / \partial V)_p$.

6. If the reaction



were to proceed at $p = 1 \text{ atm}$ and $t = 25^\circ \text{C}$, then 30 250 calories of heat would be liberated. If it is conducted in a galvanic cell, then at con-

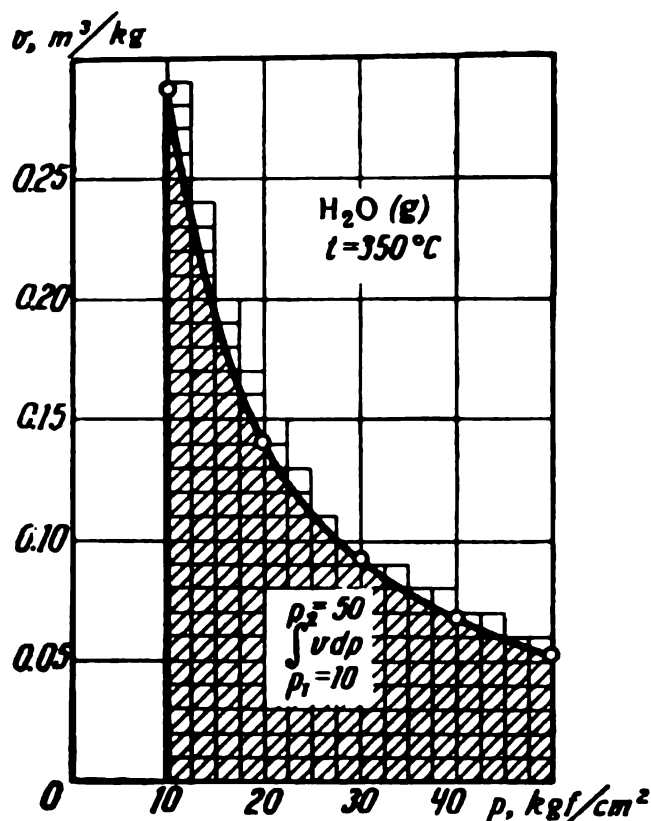


Fig. 1

* One calorie is equivalent to 41.293 atm·cm³.

stant pressure and temperature the chemical energy transforms into electric energy and the work $W' = 26\,210$ cal is performed.

Show that in both cases the change in the internal energy will be the same, and the heat different. Assume in the calculations that chlorine is an ideal gas; neglect the volume of the Ag and AgCl.

Solution. In the first case in accordance with Eq. (1.3) we have

$$Q = \Delta H = -30\,250 \text{ cal/mol}$$

and in accordance with Eq. (1.2)

$$\Delta U = \Delta H - p \Delta V \approx \Delta H - (-0.5V_{\text{Cl}_2}) \approx \Delta H + 0.5RT$$

or

$$\Delta U = -30\,250 + 0.5 \times 1.987 \times 298.2 = -30\,250 + 296 = -29\,954 \text{ cal/mol}$$

In the second case (an isobaric process) Eq. (1.3) acquires the form

$$\delta Q = dH + \delta W'$$

or

$$Q = \Delta H + W' = -30\,250 + 26\,210 = -4\,040 \text{ cal/mol}$$

Now from Eq. (1.1) we get

$$\Delta U = -4\,040 - (-296) - 26\,210 = -29\,954 \text{ cal/mol}$$

Problems

1. Show that for an adiabatic process the equation derived in solving Example 1 will become

$$pV^\gamma = \text{const}$$

and the work W can be calculated by means of the expressions

$$W = C_V (T_1 - T_2); \quad W = \frac{p_1 V_1 - p_2 V_2}{\gamma - 1};$$

$$W = \frac{p_1 V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \right]; \quad W = \frac{p_1 V_1}{\gamma - 1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} \right];$$

$$W = \frac{p_1 V_1}{\gamma - 1} \left(1 - \frac{p_2 V_2}{p_1 V_1} \right); \quad \text{and} \quad W = \frac{R}{\gamma - 1} (T_1 - T_2)$$

where

$$\gamma = \frac{C_p}{C_V}$$

In the derivation consider that $C_p - C_V = R$.

2. On the basis of the equation derived in solving Problem 1, find the work done for the adiabatic compression of 100 grammes of nitrogen at $t = 0^\circ\text{C}$, $p_1 = 1$ and $p_2 = 1.5$ atm. Assume that $C_p = 7.0 \text{ cal/mol} \cdot \text{K}$.

By how much will the work change if argon is subjected to compression? Assume that $C_p=5.0$ cal/mol·K.

3. In the synthesis of ammonia, the gas mixture before being fed into the ammonia compressor passes through a circulation pump.

Considering the compression process in the pump to be an adiabatic one and the gas mixture a diatomic ideal gas, find the temperature after compression if before it $t=15^\circ\text{C}$. The gas enters the pump under a pressure of 270 atm, and leaves it at 300 atm. Use the equation given in the conditions of Problem 1.

4. Prove that for a gas whose state is described by the van der Waals equation of state

$$\left(p + \frac{a}{V^2}\right) (V - b) = RT$$

the work of an isothermal process is calculated by the equation

$$W = RT \ln \frac{V_2 - b}{V_1 - b} - a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

What amount of heat must be removed in compressing one mole of methane from $p_1=1$ to $p_2=400$ atm to ensure an isothermal nature of the process ($t=0^\circ\text{C}$)? Use the van der Waals equation of state in the calculations; for the values of a and b for methane see Appendix 7. Find the volume of the gas before compression by the Mendeleev-Clapeyron equation, and after compression by the van der Waals equation.

5. Find the change in the internal energy in the vaporization of 1 kg of water at 150°C if the heat of vaporization equals 504.6 kcal/kg. Consider the steam to be an ideal gas and neglect the volume of the liquid.

6. The following data were obtained in studying the compressibility of ammonia ($t=275^\circ\text{C}$):

p , atm	125.4	181.0	228.2	313.9	380.0
V , cm ³ /mol	310.0	200.0	150.0	100.0	80.0

(1) calculate the work done for the isothermal compression of one mole of ammonia from $p_1=125.4$ to $p_2=380.0$ atm;

(2) is it possible to consider ammonia as an ideal gas in these conditions if the error in the data on compressibility is estimated to be 0.5%?

7. The minimum work needed to separate a mixture of ideal gases is equal to

$$W_{\min} = -pV \left(\frac{p_1}{p} \ln \frac{p}{p_1} + \frac{p_2}{p} \ln \frac{p}{p_2} + \dots \right)$$

where p_1, p_2, \dots = partial pressures of the mixture components
 V = total volume of the mixture
 p = pressure of the mixture.

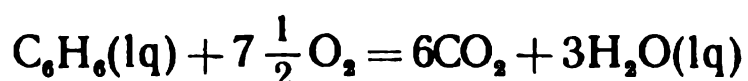
Find the minimum work needed to separate 100 m³ of air in standard conditions, considering that it consists of 20.9% O₂ and 79.1% N₂.

Express the results of the calculations in kgf/m, kWh/m³, metric hp·h/m³ and in kWh/m³ of oxygen.

8. A reservoir contains an unknown gas at 25 °C that is assumed to be nitrogen or argon. Upon the sudden expansion of 5 dm³ of the gas to a volume of 6 dm³ its temperature drops to about 0 °C. Use the equation derived in solving Example 1 to determine whether these data can serve as the basis to tell what gas the reservoir contains.

9. A reservoir with a volume of 50 dm³ contains nitrogen at $t=10$ °C and a gauge pressure of 5 atm. Find the maximum quantity of heat that can be imparted to the gas if the walls of the reservoir withstand a pressure of not over 20 atm. Use the equation derived in solving Example 1 for the calculations. In the first approximation consider that nitrogen is an ideal gas in these conditions and assume that $C_p \approx 7$ cal/mol·K.

10. The heat of combustion of benzene



at $p=1$ atm and $t=25$ °C equals 782.0 ± 1.0 kcal/mol.

Find the heat of combustion of benzene at constant volume and 25 °C, assuming that the Mendeleev-Clapeyron equation may be applied to the combustion products. Neglect the volume of the benzene and the water.

Is it possible to neglect the difference between Q_p and Q_v in this case?

Chapter Two

HEATS, HEAT CAPACITY AND ENTHALPY

2.1. HESS'S LAW

If a process proceeds irreversibly, at constant volume or constant pressure, and the products formed as a result of the process have the same temperature as the initial substances (reactants), then the heat liberated or absorbed in the process is called its *heat effect* or, more commonly, for purposes of brevity, its *heat*.

Hess' law states that the heat of a process depends only on the initial and final states of a system, i.e. on the nature of the reactants and the products and on their physical properties, and does not depend on the path of the process, i.e. on the intermediate states of the system. It is assumed that the only work is that done against external pressure*.

Using Hess's law, it is possible to compute the heat of a reaction by summing the heats of the intermediate reactions. The latter may be either actual ones, or conditional ones. Owing to the independence of the change in H (or U) on the path of transition, the intermediate steps do not enter the final result, and for this reason the question of their being possible is of no significance whatsoever.

It follows from Hess's law that:

(1) the heat of a reaction is equal to the heats of formation of the products minus the sum of the heats of formation of the reactants**;

(2) the heat of a reaction is equal to the sum of the heats of combustion of the reactants minus the sum of the heats of combustion of the products (in both cases with account taken of the stoichiometric coefficients).

The heats of different reactions (formation, combustion, solution, neutralization, etc.) are tabulated in the form of *standard heats* ΔH_{298}° (at $p=1$ atm and $t=25^\circ\text{C}$), which are usually expressed in kcal/mol or J/mol.

* Hess's law follows from the first law of thermodynamics, since the independence of $Q_V = \Delta U_V$ and $Q_P = \Delta H_P$ on the path of a process follows directly from Eqs. (1.1) and (1.3) at $\delta W' = 0$.

** Both here and in the following what is meant is the heat of formation of a compound from simple substances or elements.

In this and the following sections it is assumed, except for the few cases when the temperature is indicated, that what is had in view when dealing with heats of reaction is $\Delta H = \Delta H_{298}^\circ$ *

Examples

1. Find the heat of hydrogenation of ethylene at $T=400$ K if at this temperature the heats of formation of ethylene and ethane are equal respectively to 11.766 and -21.419 kcal/mol.

Compare the result of the calculations with $\Delta H = -32.824$ directly measured at $t=82^\circ\text{C}$ and with that of $\Delta H = -33.24$ kcal/mol found by studying the equilibrium of this reaction.

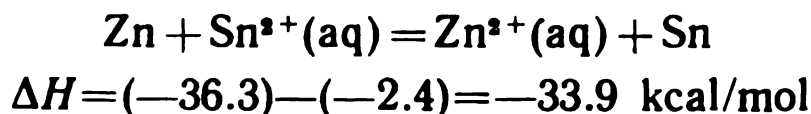
Solution. In accordance with the first corollary of Hess's law

$$\begin{aligned}\Delta H &= (\Delta H_{\text{form}})_{\text{C}_2\text{H}_6} - [(\Delta H_{\text{form}})_{\text{C}_2\text{H}_4} + (\Delta H_{\text{form}})_{\text{H}_2}] = \\ &= (-21.419) - (+11.766 + 0) = -33.185 \text{ kcal/mol}\end{aligned}$$

which differs from the values indicated by 0.361 (1.1%) and 0.055 kcal/mol (0.17%).

2. Find ΔH in the process of interaction of Zn with the ions Sn^{2+} if the heats of formation of zinc and tin ions are respectively equal to -36.3 and -2.4 kcal/mol.

Solution. For the reaction



3. Find the heat of formation of liquid *n*-heptane if its heat of combustion equals -1150.77 , and the heats of combustion of carbon and hydrogen are respectively equal to -94.052 and -68.317 kcal/mol.

Compare the result of the calculations with the value $\Delta H = -53.987$ kcal/mol.

Solution. In accordance with the second corollary of Hess's law:

$$\begin{aligned}\Delta H &= 7(\Delta H_{\text{comb}})_{\text{C}} + 8(\Delta H_{\text{comb}})_{\text{H}_2} - (\Delta H_{\text{comb}})_{\text{C}_7\text{H}_{16}} = \\ &= 7(-94.052) + 8(-68.317) - (-1150.77) = -54.13 \text{ kcal/mol}\end{aligned}$$

which differs from the value indicated in the initial conditions by 0.14 kcal/mol (0.26%).

4. The heats of solution of one mole of $\text{LiCl} \cdot \text{H}_2\text{O}$ and one mole of $\text{LiCl} \cdot 2\text{H}_2\text{O}$ are respectively equal to -4.121 and 0.981 kcal. Find the heat of hydration of the monohydrate.

Solution. In accordance with Hess's law

$$\Delta H = (-4.121) - 0.981 = -5.102 \text{ kcal/mol}$$

* When the standard heats are related to $t=18^\circ\text{C}$, they are employed together with the heats related to $t=25^\circ\text{C}$, since the difference of 7 K, as a rule, is of no practical significance.

5. On the basis of the data given below, find the heat of formation of ZnSO_4 from elements:

- (1) $\text{ZnS} = \text{Zn} + \text{S (rhomb)}$ $\Delta H_1 = 44.0 \text{ kcal/mol}$;
 (2) $2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2$ $\Delta H_2 = -221.88 \text{ kcal/mol}$;
 (3) $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ $\Delta H_3 = -46.88 \text{ kcal/mol}$;
 (4) $\text{ZnSO}_4 = \text{ZnO} + \text{SO}_3$ $\Delta H_4 = 55.1 \text{ kcal/mol}$.

Compare the result of the calculations with the most authentic value equal to -233.45 kcal/mol .

Solution. Assume that the reaction $\text{Zn} + \text{S (rhomb)} + 2\text{O}_2 = \text{ZnSO}_4$ proceeds consecutively in the following steps:

- (1) Zn and S form ZnS ($-\Delta H_1$);
 (2) ZnS is oxidized to ZnO and SO_2 ($\frac{1}{2} \Delta H_2$);
 (3) SO_2 is oxidized to SO_3 ($\frac{1}{2} \Delta H_3$);
 (4) SO_3 reacts with ZnO ($-\Delta H_4$).

(The heats of the corresponding processes are given in parentheses; a minus sign indicates that the relevant process is opposite to that given in the initial conditions.)

In accordance with Hess's law

$$\Delta H = -\Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{1}{2}\Delta H_3 - \Delta H_4 = -44.0 + (-110.94) + (-23.44) - 55.1 = -233.48 \text{ kcal/mol}$$

which practically coincides with the tabulated value.

6. With the aid of the data given in Fig. 2 (n is the number of moles of water per mole of nitric acid), calculate the heats for:

(1) the diluting of a solution containing one mole of nitric acid and 2.5 moles of water to a concentration of one mole of the acid per 9 moles of water;

(2) the two-fold dilution of 60% (weight %) nitric acid;

(3) the addition of 0.2 mole of nitric acid to one mole of a 5N solution of HNO_3 .

Solution. 1. In accordance with Hess's law

$$\Delta H_1 = -7.3 - (-5.3) = -2.0 \text{ kcal/mol}$$

2. To a concentration of 60% there corresponds

$$\frac{40}{18} : \frac{60}{63} = 2.33 \text{ moles of } \text{H}_2\text{O} \text{ per mole of } \text{HNO}_3$$

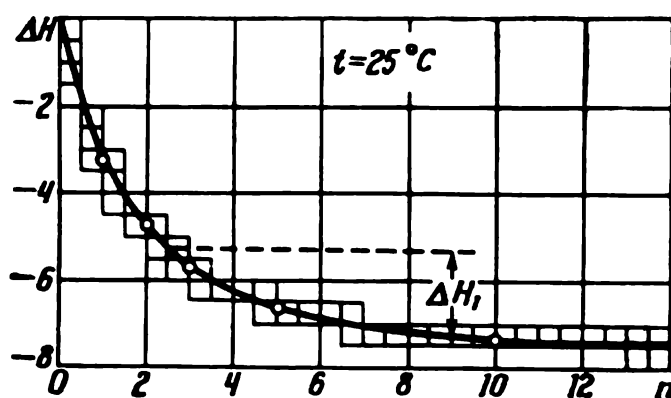


Fig. 2

and to a concentration of 30% correspondingly 8.17 moles of H_2O per mole of HNO_3 .

Consequently,

$$\Delta H_2 = (-7.25) - (-5.15) = -2.1 \text{ kcal/mol}$$

3. A 5N solution of HNO_3 contains $55.5/5 = 11.1$ moles of H_2O per mole of HNO_3 , or one mole of the solution contains $1/12.1 = 0.083$ mole of HNO_3 .

After the addition of 0.2 mole of nitric acid to one mole of this solution, the latter will contain

$$\frac{0.917}{0.083 + 0.2} = 3.24 \text{ moles of } \text{H}_2\text{O} \text{ per mole of } \text{HNO}_3$$

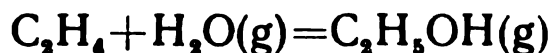
From Fig. 2 we find

$$\Delta H_3 = (-5.85) - (-7.4) = 1.55 \text{ kcal/mol}$$

Problems

1. The heats of formation of water and steam are equal respectively to -68.317 and -57.798 kcal/mol. Find the heat of vaporization of water.

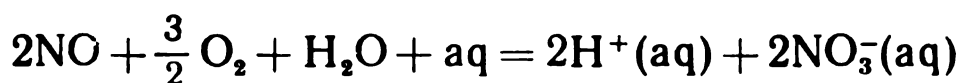
2. Find the heat of the reaction



if the heats of formation of ethylene, water vapour and gaseous ethanol are respectively 12.496 , -57.798 and -56.51 kcal/mol.

3. Calculate the heat of displacement of bromine by gaseous chlorine from a very dilute solution of sodium bromide if the heats of formation of chloride and bromide ions in an aqueous solution are respectively -39.687 and -28.67 kcal/g-ion.

4. Find the heat of the reaction



if the heats of formation of $\text{NO}_3^-(\text{aq})$, nitrogen oxide and water are respectively -49.19 kcal/g-ion, 21.6 and -68.317 kcal/mol. Assume that the heat of formation of a hydrogen ion equals zero.

5. Calculate the heat of formation of magnesium chloride in a dilute aqueous solution if the heats of formation of $\text{Mg}^{2+}(\text{aq})$ and $\text{Cl}^-(\text{aq})$ are respectively -110.23 and -39.687 kcal/g-ion.

Using the value found, determine the heat of formation of magnesium chloride in the crystalline state if its heat of solution for a dilute solution equals -36.3 kcal/mol.

6. The heat of combustion of propyl alcohol vapours is -493.3 kcal/mol.

Find the heat of combustion of liquid alcohol if its heat of vaporization according to the work of different investigators is 10–11.5 kcal/mol. Compare the result of the calculations with the tabulated value equal to -482 kcal/mol.

7. Is it possible to neglect the difference between $(Q_p)_{273}$ and $(Q_v)_{273}$ for the reaction



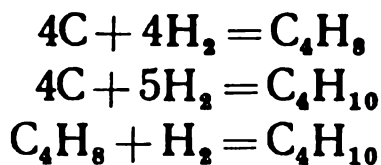
if at $t=0^\circ\text{C}$ and $p=1$ atm we have $V_{\text{CO}_2}=22\,257\text{ cm}^3$, $V_{\text{CO}}=22\,404\text{ cm}^3$, and $\rho_{\text{C}}=2.255\text{ g/cm}^3$, while the heats of combustion of carbon and carbon monoxide are respectively -94.052 ± 0.010 and -67.636 ± 0.029 kcal/mol?

8. The heat of combustion of liquid 2,2,3-trimethyl butane is 1147.97 ± 0.12 kcal/mol.

On the basis of the data given in the initial conditions of Example 3 (p. 20) find the heat of isomerization of liquid *n*-heptane into liquid 2,2,3-trimethyl butane and compare it with the experimental value of $\Delta H=-3.00\pm0.22$ kcal/mol.

9. The heats of combustion of butene-1 and *n*-butane are respectively -649.66 and -687.94 kcal/mol.

Find the heat of the reactions



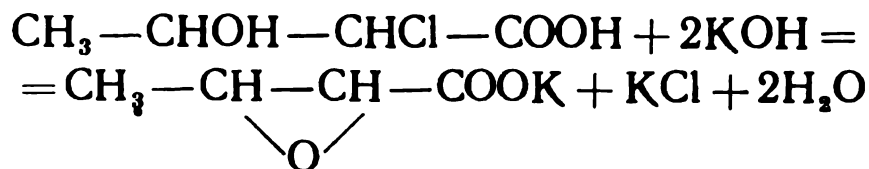
if the heats of formation of carbon dioxide and water are respectively -94.052 and -68.317 kcal/mol.

Assess the accuracy of the results of the calculations if the following experimental data have been obtained: 0.383 ± 0.180 , -29.715 and -30.09 ± 0.10 kcal/mol.

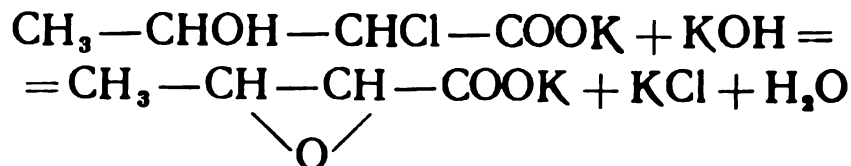
10. The heat of formation of liquid aniline ($\text{C}_6\text{H}_5\text{NH}_2$) is 7.2 kcal/mol.

Find the heat of combustion of aniline vapour if its heat of vaporization equals 104.04 cal/g, and the heats of formation of carbon dioxide and water are respectively -94.052 and -68.317 kcal/mol.

11. The heats of the reactions



and



are respectively -14.701 and 0.522 kcal/mol.

Find the heat of neutralization of chlorohydroxy-butyric acid and compare it with the experimental value of $\Delta H = -14.096$ kcal/mol.

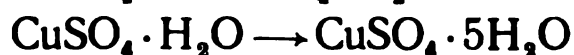
12. The heats of solution of potassium hydroxide, hydrochloric acid and potassium chloride in a very great amount of water (6400 moles of H_2O) are respectively -12.872 , -17.587 and 4.437 kcal/mol.

Find the heats of formation of these solutions from H_2O and the corresponding substances if the heats of formation of KOH , HCl and KCl are respectively -102.02 , -22.06 and -104.17 kcal/mol.

13. According to the results of solving the preceding problem, calculate the heat of neutralization of a very dilute solution of potassium hydroxide with very dilute hydrochloric acid and compare the value obtained with the experimental value (-13.75 kcal/mol). Assume the heat of formation of water to equal -68.317 kcal/mol.

14. The solution of 1 mole of $CuSO_4$, 1 mole of $CuSO_4 \cdot H_2O$ and 1 mole of $CuSO_4 \cdot 5H_2O$ in 800 moles of water is accompanied respectively by the liberation of 15.90, 9.33 and the absorption of 2.80 kcal of heat.

Find the heats of the following three processes



15. The heat of solution of 0.632 g of phenol in 135.9 g of chloroform is -0.021 , and the heat of solution of 1.569 g of phenol in 148.69 g of chloroform is -0.041 kcal.

Determine (reduced to one mole of phenol) the heat of dilution of the second solution with chloroform to the concentration of the first one.

16. The heat of neutralization of a solution containing one mole of sodium hydroxide with a solution containing one mole of nitric acid is -13.660 , and with a solution containing one mole of dichloroacetic acid is -14.830 kcal/mol.

Find the heat of dissociation of dichloroacetic acid.

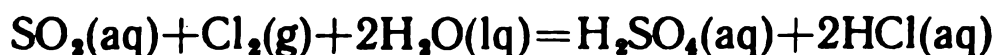
17. Find the heat of dissociation of acetic acid on the basis of the heats of formation given below (in kcal/mol). Assume that the heat of formation of water equals -68.317 kcal/mol.

Substance . . .	$NaCl(aq)$	$HCl(aq)$	$NaOH(aq)$	$CH_3COONa(aq)$
ΔH_{form} . . .	-97.166	-39.687	-112.139	-175.425
Substance . . .	$CH_3COOH(aq)$			
ΔH_{form} . . .	-117.5			

18. At $t = 25^\circ C$ the heats of formation of gaseous and liquid ammonia are -11.04 and -17.00 kcal/mol, respectively.

What is the heat of solution of liquid ammonia in 200 moles of water if the heat of solution of gaseous ammonia in the same amount of water is -8.35 kcal/mol?

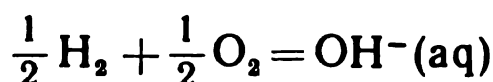
19. The heat of the reaction



at $t = 25^\circ\text{C}$ is -74.10 kcal/mol.

Using the values of the heats of formation of sulphur dioxide (-70.97), water (-68.317) and hydrogen chloride (-22.06 kcal/mol) and the heats of solution of sulphur dioxide, sulphuric acid and hydrogen chloride in a very dilute solution (respectively -8.56 , -22.05 and -17.627 kcal/mol), find the heat of formation of sulphuric acid. Compare the result of the calculations with the tabulated value of $\Delta H = -193.75$ kcal/mol.

20. Considering the heat of formation of a hydrogen ion from gaseous hydrogen to be equal to zero, find the heat of formation of the ion OH^- according to the reaction

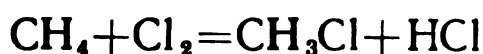


if the heat of formation of water is -68.317 kcal/mol, and its heat of dissociation into ions is 14.017 kcal/mol.

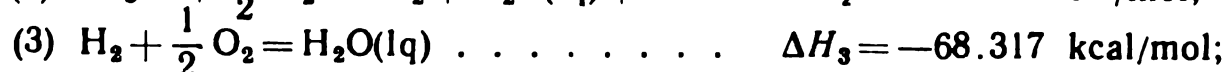
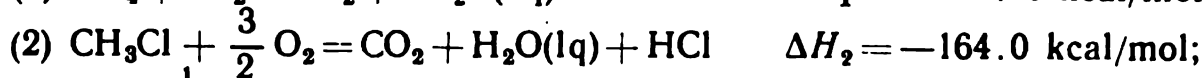
21. The heat of formation of sodium hydroxide is -101.96 , the heats of solution of sodium hydroxide and sodium oxide in a very great amount of water are respectively equal to -10.141 and -56.3 kcal/mol.

Find the heat of formation of sodium oxide if the heat of formation of water is -68.317 kcal/mol. Compare the results of the calculations with the tabulated value of $\Delta H = -99.45$ kcal/mol.

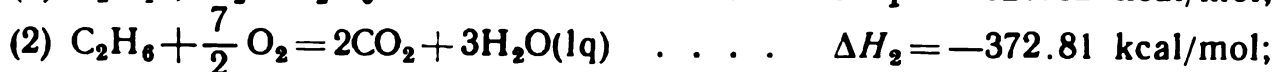
22. Find the heat of the reaction



if the heats of the following reactions are:



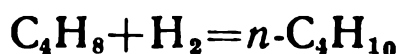
23. Find (1) the heat of formation and (2) the heat of combustion of ethylene on the basis of the following data:



24. The hypothetical heats of formation of butene-1 and n -butane in the standard state at absolute zero ΔH_0° are respectively 5.49 and

—23.25 kcal/mol. The standard enthalpies of butene-1, hydrogen and *n*-butane counted from absolute zero, $H_{400}^\circ - H_0^\circ$, are respectively 6.69, 2.731 and 7.43 kcal/mol.

Calculate the heat of the reaction of hydrogenation of butene-1



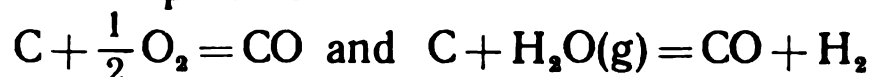
and compare the result of the calculations with the experimental value of $\Delta H = -30.341$ kcal/mol.

25. When a solution containing 1 g-eq of sodium hydroxide is added to a very dilute solution containing 1 g-eq of nitric acid and 1 g-eq of dichloroacetic acid, 13.96 kcal of heat are liberated.

In what proportion will sodium nitrate and sodium dichloroacetate be obtained? Use the data given in the initial conditions of Problem 16 for the solution.

26. What quantity of heat is liberated in the process of concentration of 100 kg of a 40.5% solution of sulphuric acid with 29% (the per cent of free SO_3) oleum to 96.1% sulphuric acid, if the heats of formation of these solutions are respectively —3.60, —9.40 and —10.00 kcal/mol?

27. When a mixture of air and steam is blown through coke, the following reactions proceed:



Determine:

(1) the air-to-steam ratio (taking the volume of steam equal to unity) ensuring isothermal proceeding of the process;

(2) how this ratio will change if it is considered that 10% of the liberated heat is lost.

Assume the heats of formation of carbon monoxide and steam to be respectively equal to —26.416 and —57.798 kcal/mol.

2.2. THERMOCHEMICAL LAWS

The *heat of formation of a gaseous substance from its elements or simple substances* can be found by the equation

$$\Delta H = \sum (n_i \varepsilon_i)_r + \sum N_i (Q_{\text{subl}})_i - \sum (n_i \varepsilon_i)_{pr} \quad (2.1)$$

where n_i and ε_i = number of bonds of a given kind and the bond breaking energy corresponding to them

N_i and $(Q_{\text{subl}})_i$ = number of atoms of crystalline elements and the heats of sublimation corresponding to them.

The subscripts “r” and “pr” respectively denote the reactants and the products of a reaction.

The *heats of formation of inorganic compounds in the crystalline state* can be calculated according to *Kapustinsky's rule*, which states that the value of ΔH_{form} for a compound of an element with other elements

of one series or one subgroup of Mendeleev's periodic table related to one gramme-equivalent is a linear function of the logarithm of the atomic number Z of the relevant element. This rule can be expressed by the following equation:

$$\frac{\Delta H_{\text{form}}}{w} \approx a \log Z + b \quad (2.2)$$

where w = valence

a and b = empirical constants

Z = atomic number of an element.

To calculate the *heats of formation of organic compounds* (in the state of an ideal gas), the empirical method proposed by Anderson, Bayer and Watson can be used. It consists in summing the corrections assigned to definite groups and bonds with account of the heats of formation of the main groups. These corrections are given in the tables in Appendix 2.

The *heats of combustion* can be determined by *Konovalov's formula*

$$\Delta H_{\text{comb}} = -(48.80 m + 10.5 n + x) \quad (2.3)$$

where m = number of atoms of oxygen needed for complete combustion of a given compound

n = number of moles of water formed

x = correction constant for the compounds of one homologous series.

For liquid compounds *Kharrash's formula* is used:

$$\Delta H_{\text{comb}} = -26.05 (4C + H - n_e) + \sum k_i \Delta_i \quad (2.4)$$

where C = number of carbon atoms

H = number of hydrogen atoms

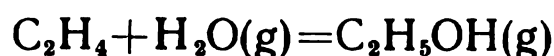
n_e = number of partly displaced electrons

k_i and Δ_i = number of identical substituents and the heat corrections for them.

Both the laws listed above and other ones, differing from one another in their degree of accuracy and the number of substances they cover, are not faultless, i.e. they can serve only for an approximate assessment of the quantities being calculated.

Examples

1. Calculate the heat of the reaction



if $\varepsilon_{\text{C-H}} = 85.6$, $\varepsilon_{\text{C=C}} = 101.2$, $\varepsilon_{\text{O-H}} = 110$, $\varepsilon_{\text{C-C}} = 62.8$ and $\varepsilon_{\text{C-O}} = 75$ kcal/mol.

Compare the result with that found from the heats of formation if $(\Delta H_{\text{form}})_{\text{C}_2\text{H}_4}^{\text{g}} = 12.56$, $(\Delta H_{\text{form}})_{\text{H}_2\text{O}}^{\text{g}} = -57.801$ and $(\Delta H_{\text{form}})_{\text{C}_2\text{H}_5\text{OH}}^{\text{g}} = -56.51$ kcal/mol.

Solution. In accordance with Eq. (2.1) we have

$$\begin{aligned}\Delta H &= (4e_{\text{C-H}} + e_{\text{C=C}} + 2e_{\text{O-H}}) - (5e_{\text{C-H}} + e_{\text{C-C}} + e_{\text{C-O}} + \\ &\quad + e_{\text{O-H}}) = (4 \times 85.6 + 101.2 + 2 \times 110) - (5 \times 85.6 + \\ &\quad + 62.8 + 75 + 110) = -12.2 \text{ kcal/mol}\end{aligned}$$

The same quantity in accordance with Hess's law can be found by using the heats of formation:

$$\Delta H = -56.51 - [12.56 + (-57.801)] = -11.27 \text{ kcal/mol}$$

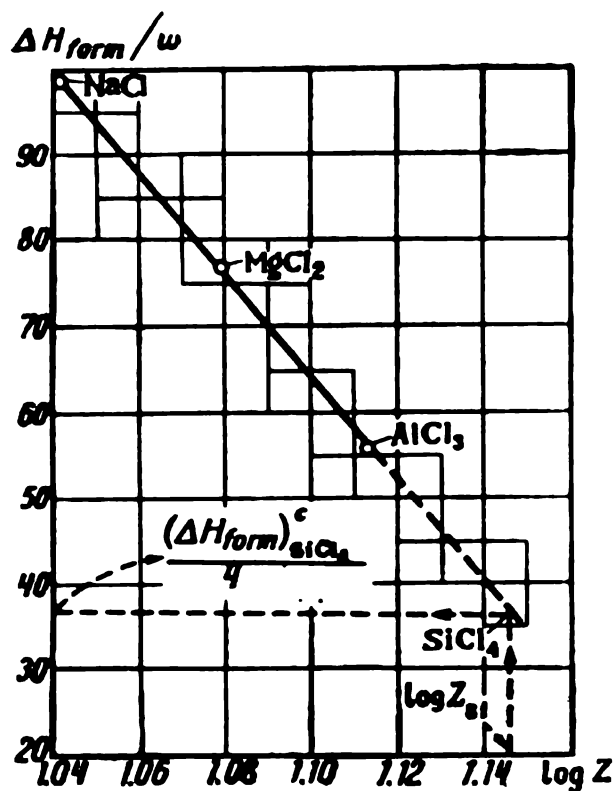


Fig. 3

The result of calculations using the bond energies differs from the accurate value by 0.93 kcal/mol (8.3%).

2. The heats of formation of sodium chloride, magnesium chloride and aluminium chloride are respectively -98.33 , -153.3 and -166.8 kcal/mol.

Find the heat of formation of silicon chloride (in the crystalline state) and compare it with the tabulated value of $\Delta H = -151.9$ kcal/mol.

Solution. The calculation may be performed either analytically or graphically. Let us use the latter procedure. For this purpose in accordance with Eq. (2.2) we plot a chart in the coordinates $\Delta H_{\text{form}}/w$

and $\log Z$ (Fig. 3). By extrapolation we find

$$\frac{(\Delta H_{\text{form}})_{\text{SiCl}_4}^c}{4} \approx 36.5$$

Consequently

$$(\Delta H_{\text{form}})_{\text{SiCl}_4}^c \approx -146$$

which differs from the tabulated value by 5.9 kcal/mol (3.9%).

By continuing the straight line, it is easy to assess the heats of formation of PCl_5 and SCl_6 (in the crystalline state).

3. Find the heats of formation (1) of gaseous ethyl chloride, and (2) of $\text{CH}_2\text{FCH}_2\text{OH(g)}$ and compare them with the tabulated values equal respectively to -25.3 and -96.6 kcal/mol.

Solution. We shall obtain the compounds which ΔH_{form} is to be calculated for artificially from the basic substance; by summation

of the corresponding corrections (see Appendix 2), we find the sought value:

	ΔH , kcal/mol
1. Basic substance (CH_4)	—17.89 (Table A)
Primary substitution of H by CH_3 group	—2.50 (Table B)
Secondary substitution of H by CH_3 group	—4.75 (Table C)
Substitution of CH_3 by chlorine	0 (Table D)
<hr/>	
$\Delta H_1 = -25.14$	
2. Basic substance (CH_4)	—17.9 (Table A)
Primary substitution of H by CH_3 group	—2.50 (Table B)
Secondary substitution of H by CH_3 group	
(A) (B)	
1 1	—4.75 (Table C)
1 2	—4.92
Substitution of CH_3 by fluorine	—35.00 (Table D)
Substitution of CH_3 by hydroxyl group	—32.70
<hr/>	
$\Delta H_2 = -97.77$	

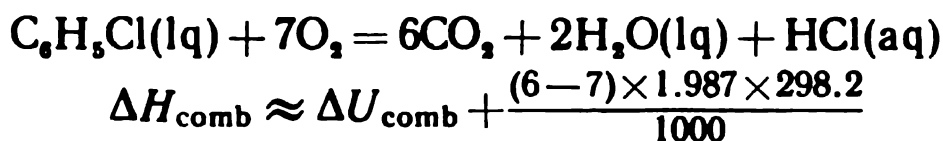
The values obtained differ from the tabulated ones by 0.16 (0.6%) and 1.17 kcal/mol (1.2%), respectively.

4. Calculate the heat of combustion of chlorobenzene with the aid of Eq. (2.4) and compare it with the experimentally found value of -735.20 ± 0.2 kcal/mol measured at constant volume if the heat correction for chlorine for aromatic compounds is -6.5 kcal/mol.

Solution. By Eq. (2.4) we have

$$\Delta H_{\text{comb}} = -26.05 (4 \times 6 + 1 \times 5 - 1) + (-6.5) = -735.9 \text{ kcal/mol}$$

Taking into account that for the reaction



we get

$$\Delta U_{\text{comb}} \approx -735.9 + 0.6 = -735.3 \text{ kcal/mol}$$

which within the limits of the error of the experiment coincides with the experimentally obtained value.

Problems

1. Calculate the heat of the reaction



according to the energies of the bonds if the heat of sublimation of carbon is 125 kcal/g-atom, $\epsilon_{\text{H-H}} = 102.6$, $\epsilon_{\text{C-H}} = 85.6$ and $\epsilon_{\text{C-C}} = 62.8$ kcal/mol.

Compare the result of the calculations with the most authentic value of $\Delta H = -20.236$ kcal/mol.

2. According to *Berkenheim's rule* (1922), the value of ΔH_{form} for a compound of an element with another one related to one gramme-equivalent is approximately equal to the arithmetical mean value of the ΔH_{form} 's for the compounds of adjacent elements (in the periodic table) with the same second element also related to one gramme-equivalent. Check this rule for silicic acid if the heats of formation of aluminium oxide and phosphorus pentoxide are respectively equal to -393.3 and -360.0 kcal/mol.

Compare the result of the calculations with the tabulated value of $\Delta H = -205.6$ kcal/mol.

3. The heats of formation of sodium bromide and magnesium bromide are respectively -86.73 and -123.9 kcal/mol.

Calculate $(\Delta H_{\text{form}})_{\text{AlBr}_3}$. Compare the result with the tabulated value equal to -123.0 kcal/mol.

4. Using the data given in Appendix 2, calculate the heats of formation of gaseous methyl acetylene and 2,3-dimethyl hexane.

Compare the results with the tabulated values correspondingly equal to 46.017 and -52.13 kcal/mol.

5. Using the data given in Appendix 2, find the heat of formation of gaseous chloral hydrate $[\text{CCl}_3\text{CH}(\text{OH})_2]$.

Compare the result with the tabulated value of $\Delta H = -103.6$ kcal/mol.

6. Using Konovalov's formula, calculate the heating value of propane if for saturated hydrocarbons $x=0$.

Compare the result with the tabulated value of $\Delta H = -530.57$ kcal/mol.

7. Find the heat of combustion of ethyl acetate if the heat correction for the bond in aliphatic esters is -16.5 kcal/mol.

Compare the result with the experimental value of $\Delta H = -538.5$ kcal/mol.

8. The following equation has been proposed to calculate the heats of combustion of liquid hydrocarbons (saturated and unsaturated ones, naphthenes, aromatic compounds, including polycondensed ones):

$$-\Delta H_{\text{comb}} = 104.2n_{\text{C}} + 26.05n_{\text{H}} + 13.0n_{=} + 46.1n_{\equiv} + \\ + 6.5n_{=c} - 3.5n_{\text{Ar-Al}} - 6.5n_{\text{Ar-Ar}}$$

where n_{C} = number of carbon atoms in a molecule

n_{H} = number of hydrogen atoms

$n_{=}$ = number of double bonds in a molecule of an olefin or in the side chains for condensed compounds

n_{\equiv} = number of triple bonds in a molecule of a hydrocarbon of the acetylene series

$n_{=c}$ = number of double bonds in a ring for naphthenes

$n_{\text{Ar-Al}}$ = number of bonds between aryl and alkyl groups

$n_{\text{Ar-Ar}}$ = number of bonds between aryl groups.

In calculations for polycondensed aromatic hydrocarbons, $n_{\text{Ar-Ar}}$ is equal to the double number of aromatic rings minus two; for example

for naphthalene $n_{\text{Ar-Ar}}=2$
 for phenanthrene $n_{\text{Ar-Ar}}=4$
 for chrysene $n_{\text{Ar-Ar}}=6$, etc.

Calculate the heat of combustion of crystalline naphthalene if $\Delta H_{\text{fus}}=4.6$ kcal/mol for it.

The experimental value ranges from -1230.4 to -1232.4 kcal/mol.

2.3. HEAT CAPACITY AND ENTHALPY

The relationship

$$\bar{C}_p \equiv \frac{\Delta H}{T_2 - T_1} \quad (2.5)$$

is called the mean isobaric heat capacity within the given interval of temperatures if the temperature in a system changes at constant pressure from T_1 to T_2 at the expense of the reception or giving up of the heat ΔH and neither phase conversion nor change in composition takes place. The mean heat capacity is related to the true heat capacity

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_p \quad (2.6)$$

by the expression

$$\bar{C}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} C_p dT \quad (2.7)$$

The dependence of C_p on T , as a rule, is expressed by equations of the kind

$$C_p = a + bT + cT^2 \quad (2.8)$$

or

$$C_p = a' + b'T + \frac{c'}{T^2} \quad (2.9)$$

where a , b , c , a' , b' and c' are empirical coefficients ($c' < 0$).

The change in the enthalpy due to a change in temperature from 0 K to T is determined on the basis of the temperature dependence of the heat capacities and the heats of phase transitions by the equation

$$H_T - H_0 = \sum \int (C_p)_i dT + \sum \Delta H_i \quad (2.10)$$

The integrals are computed graphically, while the part of the first integral covering the temperature interval from 0 K to the temperature below which there are no experimental data can be found by interpolation or correspondingly by Eqs. (2.17-2.19). If the temperature

of a substance within the limits of the given phase changes from T_1 to T_2 , then

$$H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p dT = \bar{C}_p (T_2 - T_1) \quad (2.10a)$$

If the calculations are based on spectroscopic data, then for *ideal gases* we have

$$C_p = \frac{5}{2} R + \frac{N_A}{kT^2} \left[\frac{\sum \epsilon_i^2 g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} - \left(\frac{\sum \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} \right)^2 \right] \quad (2.11)$$

and

$$H - H_0 = \frac{5}{2} RT + N_A \frac{\sum \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} \quad (2.12)$$

where N_A = Avogadro constant

k = Boltzmann constant

ϵ_i = energy of molecules on the i -th level

g_i = statistical weight.

In the majority of cases at ordinary and elevated temperatures the following equations may be used, which makes it possible to perform the calculations without data on the energy levels being available:

$$C_p = \frac{m}{2} R + R \sum_i \left(\frac{\Theta_i}{T} \right)^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T} - 1)^2} \quad (2.13)$$

$$H - H_0 = \frac{m}{2} RT + RT \sum_i \frac{\Theta_i/T}{e^{\Theta_i/T} - 1} \quad (2.14)$$

For diatomic and linear polyatomic molecules we have $m=7$ and $i=3n-5$, while for non-linear polyatomic molecules $m=8$ and $i=3n-6$; n is the number of atoms in a molecule. The characteristic temperature Θ_i is equal to

$$\Theta_i = \frac{hc}{k} \nu_i = 1.4384 \nu_i \quad (2.15)$$

where ν_i = frequency of vibrations expressed in cm^{-1}

h = Planck constant

c = velocity of light.

The terms containing $\sum f(\Theta_i/T)$ can be determined directly according to tables of the Einstein functions, which give the values of the corresponding quantities per degree of freedom (see Appendix 3).

If the frequencies of vibrations are not known, then for simple molecules satisfactory results can be obtained by the *Dobrats equation*

$$C_p = 4R + \frac{aR}{2} + \sum q_i E_{\nu_i} + \frac{3n-6-a-\sum q_i}{\sum q_i} \times \sum q_i E_{\delta_i} \quad (2.16)$$

where a = number of bonds permitting free rotation
 $\sum q_i$ = number of valence bonds in a molecule
 n = number of atoms in a molecule
 E_{γ_i} and E_{δ_i} = Einstein functions for a given bond with the characteristic frequencies of vibrations γ_i and δ_i . For the values of γ_i and δ_i for different bonds see Appendix 4, and for the values of E see Appendix 3.

The heat capacities of gases in the absence of any experimental data can be calculated using an empirical method, which consists in the summation of the corrections ascribed to definite groups of atoms and bonds (Appendix 2)*. The heat capacity of *crystalline bodies* at low temperatures is calculated for unidimensional structures (linearly polymerized substances) according to *Tarasov's equation*

$$C_V = C_1 = 19.64 \frac{T}{\Theta_1} \quad (2.17)$$

for two-dimensional structures according to *Tarasov's equation*

$$C_V = C_2 = 43.27 \left(\frac{T}{\Theta_2} \right)^2 \quad (2.18)$$

and for three-dimensional crystal lattices according to the *Debye equation*

$$C_V = C_3 = 464.5 \left(\frac{T}{\Theta_3} \right)^3 \quad (2.19)$$

The values of the Tarasov functions (C_1 and C_2) and the Debye function (C_3) are given in Appendix 5.

Examples

1. The dependence of the enthalpy of iron on the temperature is expressed by the following data:

$t, ^\circ\text{C}$	100	200	300	400	500	600
$H - H_{t=0}, \text{ cal/g-atom}$	615	1285	2015	2800	3655	4620

Find C_p graphically at $T=650$ K; compare the result with the experimental data if it is known that $(C_p)_{623}=7.82$ and $(C_p)_{673}=8.15$ cal/mol·K.

Solution. We plot a chart of $H - H_{t=0}$ versus t (Fig. 4) and draw a tangent to the curve at the point for which $t=650-273=377^\circ\text{C}$. Hence, in accordance with Eq. (2.6) we have

$$(C_p)_{650} = \left(\frac{\partial H}{\partial T} \right)_{650} \approx \frac{4160 - 760}{570 - 150} = 8.10$$

* Calculation of the heat capacity of real gases is considered in Chapters Four and Six.

Linear interpolation for the values of C_p given in the initial conditions results in the following value:

$$(C_p)_{650} = 7.82 + \frac{8.15 - 7.82}{50} \times 27 = 8.00 \text{ cal/mol}\cdot\text{K}$$

which differs from the found value by 1.3%.

2. The dependence of the molar heat capacity of acetylene on the temperature is expressed by the following experimental data:

$T, \text{ K}$	300	400	500	600	700	800	900	1000
$C_p, \text{ cal/mol}\cdot\text{K}$	9.91	11.07	12.13	13.04	13.82	14.51	15.10	15.63

- (1) Find, using the method of least squares, an equation for $C_p=f(T)$ of the kind (2.8);
- (2) check the accuracy of the equation found.

Solution. 1. The calculation consists in determining the coefficients a, b and c of Eq. (2.8) by solving the simultaneous equations

$$\begin{aligned} \sum y &= na + b \sum x + c \sum x^2 \\ \sum xy &= a \sum x + b \sum x^2 + c \sum x^3 \\ \sum x^2y &= a \sum x^2 + b \sum x^3 + c \sum x^4 \end{aligned}$$

where n is the number of measurements.

So as not to operate with very big numbers, let us introduce as the argument

$$x = \frac{T - 300}{100}$$

We enter the values of x, x^2, x^3, x^4, xy and x^2y needed to calculate the value of $y(\bar{C}_p)$ in Table 1.

Next we compile the simultaneous equations

$$105.21 = 8a + 28b + 140c$$
$$402.29 = 28a + 140b + 784c$$
$$2070.29 = 140a + 784b + 4676c$$

(a)
(b)
(c)

Excluding a from Eqs. (a) and (b), we find

$$68.11 = 84b + 588c$$

(d)

Excluding a from Eqs. (a) and (c), we get

$$458.23 = 588b + 4452c$$

(e)

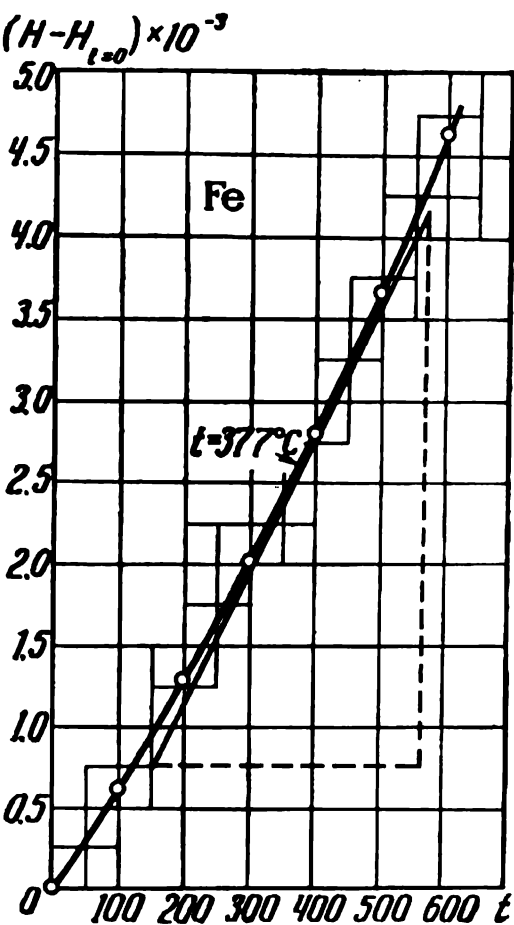


Fig. 4

Table 1

<i>T</i>	<i>y</i>	<i>x</i>	<i>x</i> ²	<i>x</i> ³	<i>x</i> ⁴	<i>xy</i>	<i>x</i> ² <i>y</i>
300	9.91	0	0	0	0	0	0
400	11.07	1	1	1	1	11.07	11.07
500	12.13	2	4	8	16	24.26	48.52
600	13.04	3	9	27	81	39.12	117.36
700	13.82	4	16	64	256	55.28	221.12
800	14.51	5	25	125	625	72.55	362.75
900	15.10	6	36	216	1296	90.60	543.60
1000	15.63	7	49	343	2401	109.41	765.87
Sum	105.21	28	140	784	4676	402.29	2070.29

From Eqs. (d) and (e) we find

$c=-0.0552$

Next we consecutively find

$b=1.197$ and $a=9.928$

whence

$C_p=9.928+1.197\frac{T-300}{100}-0.0552\left(\frac{T-300}{100}\right)^2$

or finally

$C_p=5.84+15.28\times10^{-3}T-5.52\times10^{-6}T^2$

2. Below is given a comparison of the values of C_p (cal/mol·K) computed according to the equation found in the present example with experimental ones:

<i>T</i> , K	300	400	500	600	700	800	900	1000
<i>C_p</i> (exper.)	9.91	11.07	12.13	13.04	13.82	14.51	15.10	15.63
<i>C_p</i> (calc.)	9.93	11.07	12.10	13.02	13.83	14.53	15.12	15.60

The discrepancy does not exceed 0.25%.

3. Find the consumption of heat for heating 1 kg of CdCl₂(c) from 298 to 800 K if the molar heat capacity of cadmium chloride can be expressed by the equation

$C_p=14.64+9.60\times10^{-3}T$

Solution. According to Eq. (2.10a) we have

$H_{800}-H_{298}=\int\limits_{298}^{800}(14.64+9.60\times10^{-3}T)\,dT=9990\text{ cal}$

Consequently, for heating 1 kg of CdCl₂, the following quantity of

heat is needed:

$$\frac{9990 \times 1000}{183.32 \times 1000} = 54.5 \text{ kcal}$$

4. Prove that if the temperature dependence of the enthalpy is expressed by the equation

$$H_T - H_{298} = aT + bT^2 + \frac{c}{T} + d \quad (a)$$

then the following form can be imparted to this equation:

$$\frac{[(H_T - H_{298}) - (C_p)_{298} (T - 298.2)] T}{(T - 298.2)^2} = bT + \frac{c}{298.2^2} \quad (a')$$

which makes it possible to find the constants a , b , c and d graphically according to the values of H_{T_1} , H_{T_2} and $(C_p)_{298}$.

Solution. We draw up the simultaneous equations

$$H_T - H_{298} = aT + bT^2 + \frac{c}{T} + d \quad (a)$$

$$(C_p)_{298} = a + 2 \times 298.2b - \frac{c}{298.2^2} \quad (b)$$

$$0 = 298.2a + (298.2)^2b - \frac{c}{298.2} + d \quad (c)$$

Multiplying Eq. (b) by 298.2 and subtracting Eq. (c) from it, we get

$$298.2 (C_p)_{298} = (298.2)^2b - \frac{2c}{298.2} - d \quad (d)$$

Inserting into Eq. (a) the value of d from Eq. (d) and that of a from Eq. (b), we obtain

$$H_T - H_{298} = \left[(C_p)_{298} - 596.4b + \frac{c}{298.2^2} \right] T + bT^2 + \frac{c}{T} + \left[298.2^2b - 298.2(C_p)_{298} - \frac{2c}{298.2} \right]$$

whence after transformation we find

$$H_T - H_{298} = (T - 298.2)^2b + \frac{(T - 298.2)^2c}{298.2^2T} + (C_p)_{298} (T - 298.2)$$

or after multiplication by $T/(T - 298.2)^2$ we find the sought equation. Its differentiation makes it possible to find an equation of the temperature dependence of C_p of the kind shown by Eq. (2.9).

Let us denote the left-hand part of Eq. (a') by Δ and plot a chart of Δ versus T . The points should be arranged on it along a straight line whose slope equals the coefficient b , while the length of the ordinate y_0 cut off by this line equals $c/298.2^2$. Hence in accordance with

Eqs. (a) and (d) we have

$$a = (C_p)_{298} - 2 \times 298.2b + y_0$$

and

$$d = (298.2)^2 b - 298.2(C_p)_{298} - 2 \times 298.2 y_0$$

5. Using the relationship found in Example 4, find an equation for calculating the enthalpy and heat capacity of iron, if $(C_p)_{298}$ for it equals 6.03 cal/mol·K.

Use the following data for the calculations:

T, K	400	500	600	700	800	900
$H_T - H_0, \text{ cal}$	640	1310	2050	2860	3720	4680

Solution. By means of the values of $H_T - H_0$ given in the initial conditions we determine the value of $H_T - H_{298}$, and then compute Δ :

$$\Delta = \frac{[(H_T - H_{298}) - (C_p)_{298} (T - 298.2)] T}{(T - 298.2)^2} = bT + \frac{c}{298.2^2}$$

for all the temperatures indicated in the initial conditions:

T, K	400	500	600	700	800	900
Δ	0.957	1.127	1.507	1.889	2.200	2.608

Next we plot the chart of Δ versus T (Fig. 5), and from it find the slope of the straight line:

$$b = \tan \alpha = \frac{4.0 \times 0.5}{6.1 \times 100} = \frac{2}{6100} = 0.003279$$

The length intercepted on the axis of ordinates will be

$$y_0 = \frac{c}{298.2^2} = -0.41$$

and

$$c = -0.41(298.2)^2 = -36460$$

Hence

$$a = (C_p)_{298} - 2 \times 298.2b + \frac{c}{298.2^2} = 6.03 - 596.4 \times 0.003279 + (-0.41) = 3.66$$

and

$$\begin{aligned} d &= (298.2)^2 b - 298.2(C_p)_{298} - 2 \times 298.2 \times \frac{c}{298.2^2} = \\ &= 298.2^2 \times 0.003279 - 298.2 \times 6.03 - 2 \times 298.2(-0.41) = -1262 \end{aligned}$$

Consequently, the temperature dependence of the enthalpy of iron in

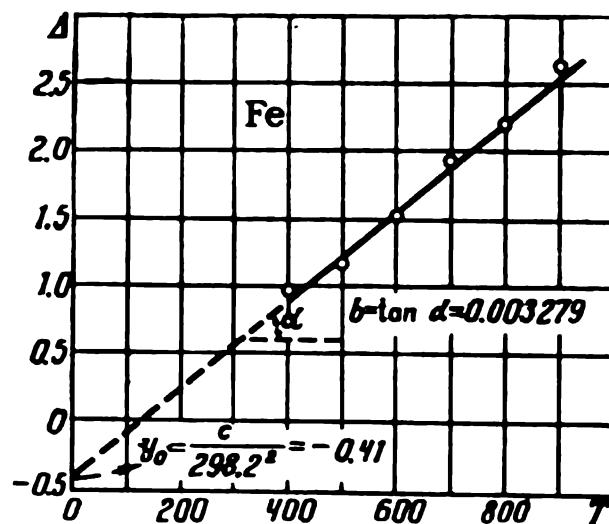


Fig. 5

the interval from 298.2 to 900 K is expressed by the equation

$$H_T - H_{298} = 3.66T + 3.279 \times 10^{-3}T^2 - \frac{0.3646 \times 10^5}{T} - 1262$$

We get the temperature dependence of C_p by differentiating this equation with respect to T

$$C_p = 3.66 - 6.558 \times 10^{-3}T + \frac{0.3646 \times 10^5}{T^2}$$

6. Calculate the heat capacity and enthalpy of carbon monoxide at 25 °C with the aid of Eqs. (2.11) and (2.12) on the basis of the distribution of the energy (in wave numbers) given in Table 2.

Table 2

Frequency of vibra- tions ν_i , cm ⁻¹	Statisti- cal weight g_i	Frequency of vibra- tions ν_i , cm ⁻¹	Statisti- cal weight g_i	Frequency of vibra- tions ν_i , cm ⁻¹	Statisti- cal weight g_i	Frequency of vibra- tions ν_i , cm ⁻¹	Statisti- cal weight g_i
0.0	1	243.2	23	931.1	45	1940	65
3.686	3	287.4	25	1016	47	2061	67
11.06	5	335.2	27	1104	49	2185	69
22.12	7	386.8	29	1196	51	2313	71
36.86	9	442.0	31	1291	53	2445	73
55.28	11	500.0	33	1390	55	2580	75
77.40	13	563.5	35	1493	57	2719	77
103.2	15	629.7	37	1599	59	2862	79
132.7	17	699.6	39	1709	61	3008	81
165.8	19	773.1	41	1823	63	3158	83
202.7	21	850.3	43				

Solution. We recalculate the values of the vibration frequencies given in the initial conditions and expressed in wave numbers into energy units (ergs per molecule). Then for each level we compute

$$g_i e^{-\epsilon_i/298.2}; \quad \epsilon_i g_i e^{-\epsilon_i/298.2} \quad \text{and} \\ \epsilon_i^2 g_i e^{-\epsilon_i/298.2}$$

and find the sums

$$\sum g_i e^{-\epsilon_i/298.2}; \quad \sum \epsilon_i g_i e^{-\epsilon_i/298.2} \quad \text{and} \\ \sum \epsilon_i^2 g_i e^{-\epsilon_i/298.2}$$

All the values are given in Table 3.

We use the results found and Eq. (2.11) to determine

$$\begin{aligned} (C_p)_{298} &= \frac{5}{2} \times 1.987 + \frac{6.023 \times 10^{23}}{(4.185 \times 10^7)(1.38 \times 10^{-16}) 298.2^2} \times \\ &\quad \times \left[\frac{37.80 \times 10^{-26}}{113.31} - \left(\frac{46.19 \times 10^{-13}}{113.31} \right)^2 \right] = \\ &= 4.968 + 1.963 = 6.931 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

Table 3

$\epsilon_i = h c \nu_i = 1.9653 \times 10^{-16} \nu_i$	$g_i e^{-\frac{\epsilon_i}{298.2}}$	$\epsilon_i g_i e^{-\frac{\epsilon_i}{298.2}} \times 10^{18}$	$\epsilon_i^2 g_i e^{-\frac{\epsilon_i}{298.2}} \times 10^{26}$
0.000	1.000	0.000	0.000
7.244×10^{-16}	2.947	0.021	0.000
2.174×10^{-15}	4.741	0.103	0.002
4.347×10^{-15}	6.294	0.274	0.012
7.244×10^{-15}	7.539	0.546	0.040
1.086×10^{-14}	8.435	0.916	0.100
1.521×10^{-14}	8.962	1.363	0.207
2.028×10^{-14}	9.136	1.853	0.376
2.608×10^{-14}	8.983	2.343	0.611
3.258×10^{-14}	8.565	2.790	0.909
3.984×10^{-14}	7.928	3.158	1.258
4.780×10^{-14}	7.146	3.415	1.632
5.648×10^{-14}	6.282	3.548	2.004
6.588×10^{-14}	5.392	3.553	2.341
7.602×10^{-14}	4.518	3.435	2.611
8.687×10^{-14}	3.704	3.218	2.795
9.844×10^{-14}	2.972	2.926	2.880
1.107×10^{-13}	2.336	2.586	2.863
1.238×10^{-13}	1.793	2.171	2.688
1.375×10^{-13}	1.352	1.859	2.556
1.519×10^{-13}	1.000	1.518	2.306
1.671×10^{-13}	0.723	1.208	2.019
1.830×10^{-13}	0.513	0.939	1.718
1.997×10^{-13}	0.356	0.711	1.420
2.170×10^{-13}	0.243	0.527	1.144
2.350×10^{-13}	0.163	0.383	0.900
2.537×10^{-13}	0.107	0.272	0.690
2.732×10^{-13}	0.069	0.189	0.516
2.934×10^{-13}	0.044	0.128	0.375
3.143×10^{-13}	0.027	0.085	0.267
3.359×10^{-13}	0.017	0.056	0.188
3.583×10^{-13}	0.010	0.035	0.125
3.813×10^{-13}	0.006	0.022	0.084
4.050×10^{-13}	0.003	0.014	0.057
4.294×10^{-13}	0.002	0.008	0.034
4.546×10^{-13}	0.001	0.005	0.023
4.805×10^{-13}	0.001	0.003	0.014
5.070×10^{-13}	0.000	0.002	0.011
5.344×10^{-13}		0.001	0.005
5.625×10^{-13}			
5.912×10^{-13}			
6.206×10^{-13}			
Sum	113.31	46.19	37.801

and from Eq. (2.12) we have

$$H_{298} - H_0 = \frac{5}{2} \times 1.987 \times 298.2 + 6.023 \times 10^{23} \times \\ \times \frac{46.19 \times 10^{-13}}{(4.185 \times 10^7) 113.31} = 2068 \text{ cal/mol}$$

Here $1/4.185 \times 10^7$ is a factor for the conversion of ergs into calories.

Check. $H_{298} - H_0 = 6.931 \times 298.2 = 2067 \text{ cal/mol}$.

7. Find the heat capacity of ethyl alcohol vapour at $t = 155^\circ\text{C}$ with the aid of Eq. (2.16). Compare the result of the calculations with the experimental value (0.447 cal/mol·K). In calculations take into account the rotation of the CH_3 group relative to the CH_2OH group.

Solution. We enter the values of γ_i , δ_i , $\sum q_i E_{\gamma_i}$ and $\sum q_i E_{\delta_i}$ for all the bonds at $T = 428$ (see Appendices 3 and 4) in Table 4.

Table 4

Bond	Number of bonds	Frequencies of vibrations		$\sum q_i E_{\gamma_i}$	$\sum q_i E_{\delta_i}$
		γ_i	δ_i		
C—C	1	989	390	1×0.8504	1×1.725
C—H	5	2914	1247	5×0.0106	5×0.5415
C—O	1	1030	205	1×0.7935	1×1.9097
O—H	1	3420	1150	1×0.0026	1×0.6439
Sum	8			1.700	6.986

In accordance with Eq. (2.16) we have

$$(C_p)_{428} = 7.95 + 0.99 + 1.700 + \frac{3 \times 9 - 6 - 1 - 8}{8} \times 6.986 = \\ = 21.12 \text{ cal/mol} \cdot \text{K} \quad (0.458 \text{ cal/g} \cdot \text{K})$$

which differs from the experimental value by 2.5%.

8. With the aid of the data given in Appendix 2 find:

- (1) the equation $C_p = f(T)$ for the vapour of acetone;
- (2) the heat capacity of acetone at $T = 376 \text{ K}$ and $T = 454 \text{ K}$ (the experimental values are 21.7 and 23.9 cal/mol·K);
- (3) the consumption of heat for heating acetone from 298.2 to 500 K.

Solution. (1) From Appendix 2 we have:

	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$
Basic substance (CH_4)	3.79	16.62	—3.24 (Table A)
First substitution	—2.00	23.20	—9.12 (Table B)
Second substitution:			
	A	B	
Straight chain 1 1 . . .	—0.49	22.04	—8.96 (Table C)
Side chains 1 2 . . .	1.09	17.79	—6.47
Ditto 1 3 . . .	1.00	19.88	—8.03
Substitution of CH_3 by $=\text{O}$. .	5.02	—66.08	30.21 (Table E)
	9.39	33.45	—5.61

Hence

$$C_p = 9.39 + 33.45 \times 10^{-3}T - 5.61 \times 10^{-6}T^2$$

(2) We calculate the heat capacity of acetone at $T=376$ and 454 K:

$$(C_p)_{376} = 9.39 + 33.45 \times 10^{-3} \times 376 - 5.61 \times 10^{-6} \times 376^2 = 21.18 \text{ cal/mol} \cdot \text{K}$$

which differs from the experimental value by 2.4%;

$$(C_p)_{454} = 9.39 + 33.45 \times 10^{-3} \times 454 - 5.61 \times 10^{-6} \times 454^2 = 23.42 \text{ cal/mol} \cdot \text{K}$$

which differs from the experimental value by 2.0%;

(3) The consumption of heat for heating the acetone is

$$\begin{aligned} H_{500} - H_{298.2} &= \int_{298.2}^{500} (9.39 + 33.45 \times 10^{-3}T - 5.61 \times 10^{-6}T^2) dT = \\ &= 9.39(500 - 298.2) + 16.73 \times 10^{-3}(500^2 - 298.2^2) - \\ &\quad - 1.87 \times 10^{-6}(500^3 - 298.2^3) = 1885 + 2898 - 184 = \\ &= 4599 \text{ cal/mol} \end{aligned}$$

9. Find an equation expressing the temperature dependence of the heat capacity of manganese chloride in the region of low temperatures. Base the calculations on the following values of the heat capacity (see Table 5).

Solution. If we compute T/C , T^2/C and T^3/C for all the values of T , it will be seen that only the second quantity is practically constant, namely, the maximum deviation from the mean value of $T^2/C = 396$ is $\pm 3\%$, which is within the limits of the error of the experiment. Consequently, manganese chloride has a laminated structure, and the temperature dependence of C for it is expressed by Eq. (2.18). Introducing the values of C and T into this equation and computing for all the temperatures the quantity

$$\sqrt{\frac{43.27}{C_2}} T$$

Table 5

T, K	C_p cal/mol·K	T, K	C_p cal/mol·K	T, K	C_p cal/mol·K
14.975	0.558	22.15	1.252	25.496	1.65
15.639	0.617	22.33	1.266	25.840	1.67
16.305	0.669	22.38	1.278	25.938	1.69
16.947	0.719	22.59	1.308	26.655	1.80
17.528	0.775	22.65	1.310	26.987	1.84
18.047	0.818	22.86	1.322	27.206	1.87
18.515	0.859	23.11	1.359	27.538	1.90
18.945	0.894	23.15	1.366	27.955	1.97
19.345	0.933	23.54	1.397	28.347	2.05
19.844	0.972	23.71	1.410	28.722	2.09
20.356	1.02	23.94	1.442	29.288	2.16
20.81	1.11	24.32	1.496	29.806	2.24
21.23	1.15	24.51	1.496	30.298	2.31
21.27	1.16	24.69	1.531	30.762	2.38
21.62	1.20	24.932	1.541	31.204	2.51
21.66	1.208	25.126	1.571	31.620	2.60
21.91	1.228	25.136	1.579	32.27	2.63
21.99	1.231	25.316	1.592	32.50	2.65

we find

$$(\Theta_s)_{\text{MnCl}_2} \approx 324$$

Hence

$$C_{\text{MnCl}_2} = 43.27 \left(\frac{T}{324} \right)^2$$

or

$$C_{\text{MnCl}_2} = 4.12 \times 10^{-4} T^2$$

Problems

1. The heat capacity of crystalline sodium hydroxide within the temperature interval from 298 to 595 K can be assumed equal to 19.2; the heat capacity of liquid sodium hydroxide within the interval from 595 to 900 K can be assumed equal to 20.4 cal/mol·K.

Find the consumption of heat for the isobaric heating of 1 kg of sodium hydroxide from 298 to 700 K if $\Delta H_{\text{fus}} = 2000$ cal/mol and $T_{\text{fus}} = 595$ K.

2. Is it possible to use the Dulong and Petit law in combination with the principle of additivity to calculate $(C_p)_{298}$ for nickel chloride (the atomic heat capacity is 6.2 cal) if the temperature dependence of the molar heat capacity for this compound is approximately expressed by the equation

$$C_p = 13.10 + 13.1 \times 10^{-3} T$$

3. The temperature dependence of the molar enthalpy of tin dioxide within the interval from 298 to 1500 K can be expressed by the equation

$$H_T - H_{298} = 17.66T + 1.20 \times 10^{-3}T^2 + \frac{5.16 \times 10^5}{T} - 7103$$

Find the equation of the temperature dependence of C_p .

Calculate $(C_p)_{500}$.

Compare the result with the value of $C_p = 16.98$ cal/mol·K.

4. The temperature dependence of the molar heat capacity for silver sulphide within the interval from 298 to 452 K can be expressed by the equation

$$C_p = 10.13 + 26.4 \times 10^{-3}T$$

Find the mean heat capacity within the indicated temperature interval.

5. The heat capacity of magnesium fluoride is:

$t, ^\circ\text{C}$	300	400	500	600	700	800	900	1000
C_p , cal/mol·K	16.79	17.99	19.22	20.48	21.78	23.11	24.47	25.84

Find the temperature dependence of C_p with the aid of the method of mean values using the relationship

$$C_p = a + bT$$

6. The molar heat capacity of carbon monoxide is expressed by the following data:

T , K	300	500	700	900	1500	2000
C_p , cal/mol·K	6.96	7.11	7.43	7.75	8.36	8.59

Find $H_{2000} - H_{500}$ by the method of graphical integration.

7. The temperature dependence of the molar heat capacity for $\text{Ca}_3(\text{PO}_4)_2$ can be expressed by the equation

$$C_p = 48.59 + 40.66 \times 10^{-3}T - \frac{6.24 \times 10^5}{T^2}$$

which is true with an accuracy of 2% within the interval from 273 to 1373 K.

Find the change in the enthalpy when this substance is heated from $t_1 = 600$ to $t_2 = 900$ °C.

8. The temperature dependence of the heat capacity of diatomic sulphur can be expressed by the equation

$$C_p = 8.63 + 0.26 \times 10^{-3}T - \frac{0.84 \times 10^5}{T^2}$$

1. Find the equation $H_T - H_{273} = f(T)$.

2. Calculate $H_{1000} - H_{273}$.

9. For gaseous phosphorus $H_{500} - H_{298} = 1620$ and $H_{1000} - H_{298} = 5910$.

Determine:

(1) with the aid of the equation derived in solving Example 4, the relationships

$$H_T - H_{298} = f(T) \text{ and } C_p = f'(T)$$

if $(C_p)_{298} = 7.65 \text{ cal/mol} \cdot \text{K}$;

(2) the consumption of heat for heating one mole of gaseous phosphorus from $T_1 = 600$ to $T_2 = 900 \text{ K}$.

10. Use Eq. (2.13) to calculate the heat capacity of carbon monoxide at $T = 1000 \text{ K}$ if $\Theta_{\text{CO}} = 3085$.

Compare the result with the value calculated from tabulated data (Appendix 3).

11. Find the enthalpy of carbon monoxide at 25°C . Use Eq. (2.14) for calculations.

Compare the result of the calculations with that obtained in solving Example 6.

12. The frequencies of vibrations in a molecule of hydrogen sulphide are

$$\nu_1 = 1260 \text{ cm}^{-1} \text{ and } \nu_2 = \nu_3 = 2620 \text{ cm}^{-1}$$

Calculate the heat capacity of this substance at 25°C :

(1) with the aid of Eq. (2.13);

(2) according to tables of the Einstein functions (Appendix 3).

Compare the results with the experimentally found value of $C_p = 8.149 \text{ cal/mol} \cdot \text{K}$.

13. Calculate C_p for gaseous benzene by Eq. (2.16) at $T = 410 \text{ K}$ and compare the result with the experimental value of $C_p = 27.3 \text{ cal/mol} \cdot \text{K}$.

14. With the aid of the data given in Appendix 2:

(1) find the equation of the temperature dependence of C_p for gaseous 2,2,4-trimethyl pentane;

(2) calculate the heat capacity of this substance at $T = 442 \text{ K}$ and compare it with the experimental value of $C_p = 64.2 \text{ cal/mol} \cdot \text{K}$.

15. The heat capacity of arsenic trioxide at $t = -213.0^\circ\text{C}$ is 5.839 and at $t = -130.2^\circ\text{C}$ is $13.80 \text{ cal/mol} \cdot \text{K}$. What is the structure of this compound?

16. For aluminium $\Theta = 390$. Using the data given in Appendix 5, find the heat capacity of aluminium at $T = 37.2 \text{ K}$ and compare it with the experimental value equal to $0.396 \text{ cal/g-atom} \cdot \text{K}$.

17. The following equation was proposed for the temperature dependence of the heat capacity of potassium chloride

$$C_p = 12.64 + 1.35 \times 10^{-3} T - \frac{0.67 \times 10^5}{T^2}$$

Can this dependence be expressed with the aid of the equation

$$C_v = f\left(\frac{T}{\Theta}\right)$$

Assume that the relationship between C_p and C_v is expressed by the equation

$$C_p \approx C_v + 0.0214 C_v^2 \frac{T}{T_{\text{fus}}} \quad \text{and} \quad (T_{\text{fus}})_{\text{KCl}} = 1063$$

2.4. THEORETICAL TEMPERATURE OF COMBUSTION

If the initial temperature of a substance being burned is t_0 , and the temperature of the other substances (for example oxygen and various inert gases) is t_1 , t_2 , etc., then assuming that the reactants had been cooled to 0°C and the reaction was then conducted, we have

$$\sum \int_{273}^{T_x} (C_p)_r dT + Q_{273} = \sum \int_{273}^{T_x} (C_p)_{\text{pr}} dT \quad (2.20)$$

where $(C_p)_r$ = heat capacity of reactants

$(C_p)_{\text{pr}}$ = heat capacity of products of reaction (including the inert admixtures and a possible excess amount of oxygen)

T_x = theoretical temperature of combustion, i.e. the temperature of complete and adiabatic combustion.

When dealing with an explosive reaction, the equation of the heat balance (2.20) will include Q_v and C_v , respectively.

For purposes of simplification, the standard heat may be used instead of Q_{273} and the mean heat capacities (Appendix 6) instead of the true ones, $t=25^\circ\text{C}$ being taken as the lower limit. Here the errors, as a rule, will not be beyond the limits of the error in the high-temperature values of the heat capacity.

If the temperature is very high, a correction for dissociation of the combustion products is introduced in accurate calculations. It should be taken into account here that in flue gases the dissociation will be much more considerable than what follows from tabulated data, since the partial pressure of the gases is not great.

Examples

1. Find the theoretical temperature of combustion of carbon monoxide with the theoretically needed amount of air if the initial temperature is 25°C , the pressure $p=1$ atm, and the temperature dependence of C_p for carbon dioxide and nitrogen within the interval from 298 to 2500 K with an accuracy of about 1-1.5% is expressed by the equa-

tions

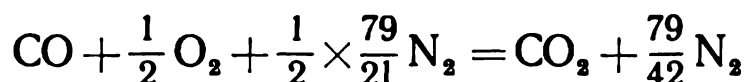
$$(C_p)_{\text{CO}_2} = 10.55 + 2.16 \times 10^{-3}T - \frac{2.04 \times 10^5}{T^2}$$

$$(C_p)_{\text{N}_2} = 6.66 + 1.02 \times 10^{-3}T$$

The standard heats of formation of CO and CO₂ are respectively —26.416 and —94.052 kcal/mol.

Assume that air consists of 79% by volume of nitrogen and 21% by volume of oxygen. Neglect the dissociation of the carbon dioxide.

Solution. The heat of the reaction of combustion of carbon monoxide



equals —94 052—(—26 416)=—67 636 cal; owing to the adiabatic nature of the process, it is used to heat one mole of carbon dioxide and 79/42 moles of nitrogen. Hence

$$67\,636 = \int_{298}^T (C_p)_{\text{CO}_2} dT + \frac{79}{42} \int_{298}^T (C_p)_{\text{N}_2} dT$$

or

$$67\,636 = \int_{298}^T (10.55 + 2.16 \times 10^{-3}T - 2.04 \times 10^5 T^{-2}) dT +$$

$$+ \frac{79}{42} \int_{298}^T (6.66 + 1.02 \times 10^{-3}T) dT$$

or

$$67\,636 = 10.55(T - 298.2) + \frac{2.16 \times 10^{-3}}{2} (T^2 - 298.2^2) -$$

$$- 2.04 \times 10^5 \left(-\frac{1}{T} + \frac{1}{298.2} \right) + \frac{79}{42} \times 6.66 (T - 298.2) +$$

$$+ \frac{79}{42} \times 0.51 \times 10^{-3} (T^2 - 298.2^2)$$

After transformation we get

$$0.002\,039\,3T^3 + 23.08T^2 - 75\,398T + 204\,000 = 0$$

We determine the theoretical temperature of combustion by the method of trial and error.

We assume that $T=2700$ K. Hence

$$40\,139\,000 + 168\,250\,000 - 205\,860\,000 + 204\,000 = 2\,733\,000 \neq 0$$

We assume that $T=2600$ K. Hence

$$35\,842\,000 + 156\,020\,000 - 198\,240\,000 + 204\,000 = -6\,174\,000 \neq 0$$

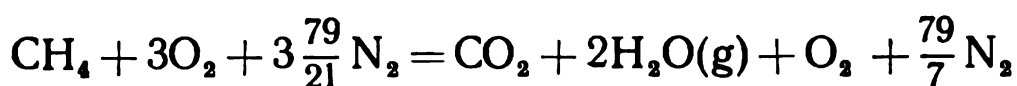
We assume that $T=2650$ K. Hence

$$37\,952\,000 + 162\,090\,000 - 202\,050\,000 + 204\,000 = -1\,804\,000 \neq 0$$

By interpolation we find that $T \approx 2670$ K.

2. Calculate the theoretical temperature of combustion of methane with a 150% excess of air if the temperature of the methane and air is 0°C . Assume that $\Delta H_{273} \approx \Delta H_{298}$ and use the mean heat capacities (see Appendix 6). The standard heat of combustion of methane equals $-212\,790$ cal/mol.

Solution. The equation of the combustion process has the form



Hence

$$\begin{aligned} 212\,790 &= (\bar{C}_p)_{\text{CO}_2}(T-273) + 2(\bar{C}_p)_{\text{H}_2\text{O}}^{\text{g}}(T-273) + \\ &+ (\bar{C}_p)_{\text{O}_2}(T-273) + \frac{79}{7}(\bar{C}_p)_{\text{N}_2}(T-273) = \\ &= \left[(\bar{C}_p)_{\text{CO}_2} + 2(\bar{C}_p)_{\text{H}_2\text{O}}^{\text{g}} + (\bar{C}_p)_{\text{O}_2} + \frac{79}{7}(\bar{C}_p)_{\text{N}_2} \right] \times (T-273) \end{aligned}$$

Assume that $t = 1700^\circ\text{C}$. Therefore

$$\left(12.75 + 2 \times 10.09 + 8.28 + \frac{79}{7} \times 7.86 \right) \times 1700 \approx 220\,900 \text{ cal}$$

which exceeds $212\,790$ cal.

Assume that $t = 1600^\circ\text{C}$. Therefore

$$\left(12.66 + 2 \times 9.96 + 8.24 + \frac{79}{7} \times 7.82 \right) \times 1600 \approx 206\,500 \text{ cal}$$

which is less than $212\,790$ cal.

By linear interpolation we find

$$t = 1642^\circ\text{C}$$

3. How can the fact be explained that the theoretical temperature of combustion of different gases in air (without an excess amount of the latter) is approximately the same, notwithstanding the fact that their heating values differ considerably from one another?

Solution. This is explained by the circumstance that gases having a higher heating value form a greater amount of combustion products with a higher heat capacity.

4. What will be the form of the heat balance equation if we use the heat at the temperature of the reaction (Q_T) instead of Q_{273} (or Q_{298})?

Solution. In this case the equation of the heat balance will acquire the form

$$Q_T = \sum n_i (\bar{C}_p)_i (t - t_i)$$

where \bar{C}_{p_i} are the mean heat capacities in the relevant temperature interval.

The calculations using this equation are complicated, since for this purpose it is necessary to compute Q_T and the values of $(C_p)_i (t-t_i)$ for all the substances [it should be noted that all the quantities in Eq. (2.20) are tabulated].

5. A mixture of one mole of hydrogen and the theoretical amount of air is exploded in a closed vessel at $t=25^\circ\text{C}$ and $p=1$ atm.

Find:

- (1) the maximum temperature in the explosion;
- (2) the maximum pressure.

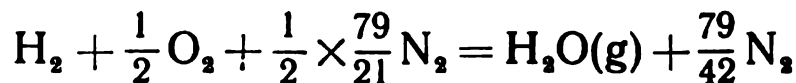
The heat of water vapour formation at $t=25^\circ\text{C}$ and $p=1$ atm is -57.798 kcal/mol.

For simplification use the values of the mean heat capacities for the calculations (see Appendix 6) and consider the components of the reaction to be ideal gases.

Solution. (1) In accordance with Eq. (1.2), the heat of combustion of hydrogen at $V=\text{const}$ is

$$\Delta U = \Delta H - (1 - 1.5)RT = -57\,798 + 0.5 \times 1.987 \times 298.2 \approx -57\,500 \text{ cal/mol}$$

This heat is spent for heating the reaction products



Since the explosion is an adiabatic process, then

$$57\,500 = \int_{298}^T (C_V)_{\text{H}_2\text{O}} dT + \frac{79}{42} \int_{298}^T (C_V)_{\text{N}_2} dT$$

or

$$57\,500 = [(\bar{C}_p)_{\text{H}_2\text{O}} - R](T - 298) + \frac{79}{42} [(\bar{C}_p)_{\text{N}_2} - R](T - 298)$$

Assume that $t=2825^\circ\text{C}$. Hence in accordance with the data given in Appendix 6, we have

$$(11.11 - 1.987) \times 2800 + \frac{79}{42} (8.22 - 1.987) \times 2800 = 58\,380 \text{ cal/mol}$$

which is greater than the value of ΔU .

Assume that $t=2725^\circ\text{C}$. Now

$$(11.03 - 1.987) \times 2700 + \frac{79}{42} (8.19 - 1.987) \times 2700 = 55\,895 \text{ cal/mol}$$

which is smaller than the value of ΔU .

By linear interpolation we find that $t \approx 2790^\circ\text{C}$.

Further precisising is not expedient, since the result is a first approximation: at $t=3000^\circ\text{C}$ the degree of dissociation of steam is about 16%.

(2) In accordance with the Mendeleev-Clapeyron equation

$$p = \sum n \frac{RT}{V}$$

Since

$$V_1 = V_2 \quad (V = \text{const})$$

then

$$\frac{p_2}{p_1} = \frac{\sum n_2}{\sum n_1} \cdot \frac{T_2}{T_1}$$

where the subscripts "1" and "2" correspond to the initial and the final states (before and after the explosion).

Consequently

$$p_2 = p_1 \frac{\sum n_2}{\sum n_1} \frac{T_2}{T_1} = 1 \times \frac{1 + \frac{79}{42}}{1 + \frac{1}{2} + \frac{79}{42}} \times \frac{3000}{298} = \frac{1 + 1.881}{1 + 0.5 + 1.881} \times \frac{3000}{298} \approx 8.5$$

Problems

1. Determine the approximate value of the theoretical temperature of combustion of carbon monoxide with the theoretical amount of air if the initial temperature is 25 °C and the pressure is $p = 1$ atm. Use the table of mean heat capacities (Appendix 6) for the calculations. Neglect the dissociation of the carbon dioxide. Assume that air consists of 21% by volume of oxygen and 79% of nitrogen respectively. Compare the result of the calculations with that obtained in solving Example 1.

2. By how much will the temperature of combustion found in solving Example 2 change if it is considered that owing to incomplete combustion and radiation losses about 80% of the heat is utilized?

3. By how much will the theoretical temperature of combustion change for the case considered in Example 2 if the air is heated to 200 °C?

4. What temperature should methane and air be heated to for the theoretical temperature of combustion to equal 2000 °C in the conditions of Example 2?

5. By how much will the theoretical temperature of combustion change for the case considered in Example 2 if the air used has been enriched with oxygen up to 30% by volume?

2.5. INFLUENCE OF TEMPERATURE ON HEAT OF REACTION

The temperature dependence of the heat of a reaction (Q_p or Q_v) is expressed by the equation

$$\frac{\partial Q}{\partial T} = \Delta C \quad (2.21)$$

where ΔC is the difference between the sums of the heat capacities (C_p or C_v) for the products and the reactants taken with account of the stoichiometric coefficients.

Since processes most often proceed at a constant pressure, the form of Eq. (2.21) customarily used is the one in which $Q=Q_p=\Delta H$ and $\Delta C=\Delta C_p$. In this case integration of Eq. (2.21) yields

$$\Delta H_T - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p dT \quad (2.22)$$

If the temperature dependence of C_p is expressed by the power series (2.8) and (2.9), then

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \frac{\Delta c'}{T^2} \quad (2.23)$$

In this equation Δa , Δb , Δc and $\Delta c'$ are the differences between the sums of the relevant coefficients in the heat capacity equations for the products and the reactants (taken with account of the stoichiometric coefficients), the values of Δc relating to the substances whose heat capacity is expressed by Eq. (2.8), and of $\Delta c'$ to those whose heat capacity is expressed by Eq. (2.9).

After using Eq. (2.23) in Eq. (2.21) and integrating, we get the equation

$$\Delta H_T = \Delta H_0 + \Delta aT + \frac{1}{2} \Delta bT^2 + \frac{1}{3} \Delta cT^3 - \frac{\Delta c'}{T} \quad (2.24)$$

where ΔH_0 is an integration constant.

If the mean heat capacities of the reactants are to be used, then in accordance with Eq. (2.21) we obtain

$$\Delta H_{T_2} = \Delta H_{T_1} + (\Delta \bar{C}_p)_{T_1 \text{ to } T_2} (T_2 - T_1) \quad (2.25)$$

To calculate ΔH it is necessary to know:

(1) the temperature dependence of the heat capacity for all the reactants;

(2) the heat of the reaction at one temperature, for example, the standard heat ΔH_{298}° ; here both the known heat and the one being determined should relate to the temperature interval for which the equations $C_p=f(T)$ are true.

The calculation can be performed analytically or graphically. When the algebraic expression for $C_p=f(T)$ is unknown or when it is difficult to select, it is preferable to determine the right-hand part of Eq. (2.22) by graphical integration. Other methods of calculating the temperature dependence of the heats of chemical reactions are considered in Chapter Nine. (For the influence of the temperature on the heat of phase transformations see Chapter Five.)

Examples

1. The heats of solution of one mole of KCl in 200 moles of water at $p=1$ atm are:

$t, ^\circ\text{C}$	21	23
$\Delta H, \text{ cal}$	4339	4260

Determine ΔH_{298} and compare it with the experimental value of 4194 cal/mol.

Solution. Since the temperature interval in which the heat is measured is very small, the temperature coefficient of the heat $(\partial\Delta H/\partial T)_p$ can be considered as a constant quantity; hence in accordance with Eq. (2.21) we have

$$\Delta C_p = \frac{4260 - 4339}{23 - 21} = -39.5 \text{ cal/mol} \cdot \text{K}$$

whence by Eq. (2.22)

$$\Delta H_{298} = 4260 + (-39.5) \times 2 = 4181 \text{ cal/mol}$$

The found value of ΔH_{298} differs from the value given in the initial conditions of the example by 13 cal (0.31%).

2. The heat of hydration of butene-1 at 82°C is $-30\,341$ cal/mol. The heat capacities of the reactants are known at 298.2 and 400 K (in cal/mol·K):

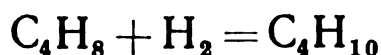
$T, \text{ K}$	298.2	400
$(C_p)_{\text{C}_4\text{H}_8}$	21.35	26.94
$(C_p)_{\text{H}_2}$	6.892	6.974
$(C_p)_{\text{C}_4\text{H}_{10}}$	23.61	29.80

Find ΔH_{298} , assuming that

$$(\Delta C_p)_{355} = \frac{1}{2} [(\Delta C_p)_{298} + (\Delta C_p)_{400}]$$

Compare the result with the value computed from the heats of formation if $(\Delta H_{\text{form}})_{\text{C}_4\text{H}_{10}} = -29\,812$ and $(\Delta H_{\text{form}})_{\text{C}_4\text{H}_8} = 280$ cal/mol.

Solution. For the reaction



$$(\Delta C_p)_{400} = 29.80 - 26.94 - 6.974 = -4.114 \text{ cal/mol} \cdot \text{K}$$

and

$$(\Delta C_p)_{298} = 23.61 - 21.35 - 6.892 = -4.632 \text{ cal/mol} \cdot \text{K}$$

hence

$$(\Delta C_p)_{355} = \frac{(-4.114) + (-4.632)}{2} = -4.373 \text{ cal/mol} \cdot \text{K}$$

Consequently, in accordance with Eq. (2.22)

$$\begin{aligned} \Delta H_{298} &= \Delta H_{355} + \Delta C_p (298.2 - 355) = -30\,341 + \\ &+ (-4.373) \times (-56.8) = -30\,341 + 248 = -30\,093 \text{ cal/mol} \end{aligned}$$

Calculation according to the heats of formation on the basis of Hess's law gives the same result:

$$\Delta H_{298} = (-29\,812) - 280 = -30\,092 \text{ cal/mol}$$

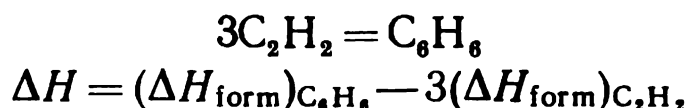
3. The heats of formation of gaseous acetylene and benzene are equal to (in cal/mol):

$T, \text{ K}$	1 000	1 100	1 200	1 300	1 400
$\Delta H_{\text{C}_2\text{H}_2}$	53 304	53 151	53 003	52 851	52 698
$\Delta H_{\text{C}_6\text{H}_6}$	14 818	14 630	14 520	14 450	14 410

Find the heat capacity of benzene vapour at $T=1200 \text{ K}$ if at this temperature $(C_p)_{\text{C}_2\text{H}_2} = 16.744 \text{ cal/mol} \cdot \text{K}$.

Compare the result with the exact value of $C_p = 53.860 \text{ cal/mol} \cdot \text{K}$.

Solution. According to Hess's law for the reaction



We calculate the values of ΔH :

$T, \text{ K}$	1000	1100	1200	1300	1400
$\Delta H, \text{ cal}$	-145 094	-144 829	-144 489	-144 103	-143 684

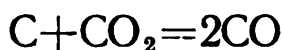
Next we plot a chart of ΔH versus T and by graphical differentiation find that at $T=1200 \text{ K}$ we have $(\partial\Delta H/\partial T)_p = 3.6 \text{ cal/mol} \cdot \text{K}$. Consequently, at $T=1200 \text{ K}$

$$(C_p)_{\text{C}_6\text{H}_6} - 3(C_p)_{\text{C}_2\text{H}_2} = 3.6 \text{ and}$$

$$(C_p)_{\text{C}_6\text{H}_6} = 3 \times 16.744 + 3.6 = 53.83 \text{ cal/mol} \cdot \text{K}$$

which differs from the exact value by 0.06%.

4. Find the equation $\Delta H = f(T)$ for the reaction



if the heats of combustion of C and CO are respectively $-94\,052$ and $-67\,636 \text{ cal/mol}$, and the temperature dependence of the heat capacity is expressed by the following equations:

$$(C_p)_{\text{C}} = 2.673 + 2.617 \times 10^{-3}T - \frac{1.169 \times 10^5}{T^2}$$

$$(C_p)_{\text{CO}_2} = 6.369 + 10.100 \times 10^{-3}T - 3.405 \times 10^{-6}T^2$$

$$(C_p)_{\text{CO}} = 6.25 + 2.091 \times 10^{-3}T - 0.459 \times 10^{-6}T^2$$

Compute the value of ΔH_{1000} and compare the result with the most accurate value of $\Delta H_{1000} = 40\,781 \text{ cal/mol}$.

Solution. For the reaction being considered we have

$$\Delta a = 2 \times 6.25 - (6.369 + 2.673) = 3.458$$

$$\Delta b = [2 \times 2.091 - (10.100 + 2.617)] \times 10^{-3} = -8.535 \times 10^{-3}$$

$$\Delta c = [2(-0.459) - (-3.405)] \times 10^{-6} = 2.487 \times 10^{-6}$$

$$\Delta c' = 0 - (-1.169 \times 10^5) = 1.169 \times 10^5$$

Therefore in accordance with Eq. (2.23)

$$\Delta C_p = 3.458 - 8.535 \times 10^{-3}T + 2.487 \times 10^{-6}T^2 + \frac{1.169 \times 10^5}{T^2}$$

We find the value of the heat needed for calculations using Hess's law:

$$\Delta H_{298} = -94\,052 - 2(-67\,636) = 41\,220 \text{ cal/mol}$$

Next by Eq. (2.24) we calculate the integration constant ΔH_0 :

$$41\,220 = \Delta H_0 + 3.458 \times 298.2 - 4.2675 \times 10^{-3} \times 298.2^2 + \\ + 0.829 \times 10^{-6} \times 298.2^3 - \frac{1.169 \times 10^5}{298.2}$$

whence

$$\Delta H_0 = 40\,938 \text{ cal/mol}$$

Consequently, the equation $\Delta H = f(T)$ for the process being considered has the form

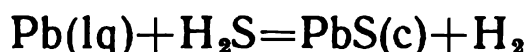
$$\Delta H = 40\,938 + 3.458T - 4.2675 \times 10^{-3}T^2 + \\ + 0.829 \times 10^{-6}T^3 - \frac{1.169 \times 10^5}{T}$$

According to the derived equation we find

$$\Delta H_{1000} = 40\,841 \text{ cal/mol}$$

This value differs from the most accurate one by 0.15% (60 cal), which is within the limits of the accuracy of the equations $C_p = f(T)$.

5. Find the temperature dependence of the heat of the reaction



and compute ΔH_{1223} , if

$$(C_p)_{\text{Pb}}^c = 5.72 + 2.08 \times 10^{-3}T$$

$$(C_p)_{\text{H}_2\text{S}} = 7.00 + 3.75 \times 10^{-3}T$$

$$(C_p)_{\text{PbS}}^c = 10.63 + 4.61 \times 10^{-3}T$$

$$(C_p)_{\text{H}_2} = 6.65 + 0.69 \times 10^{-3}T$$

$$(\Delta H_{298})_{\text{PbS}} = -22\,500 \text{ cal/mol}; \quad (\Delta H_{298})_{\text{H}_2\text{S}} = -4800 \text{ cal/mol}$$

$$(T_{\text{fus}})_{\text{Pb}} = 600.5 \text{ K}; \quad (\Delta H_{\text{fus}})_{\text{Pb}} = 1224 \text{ cal} \quad \text{and}$$

$$(C_p)_{\text{Pb}}^{\text{liq}} = 6.8 \text{ cal/mol} \cdot \text{K}$$

Solution. For the reaction $\text{Pb(c)} + \text{H}_2\text{S} = \text{PbS(c)} + \text{H}_2$ we have

$$\Delta C_p = 4.56 - 0.53 \times 10^{-3} T$$

and

$$\Delta H = \Delta H_0 + 4.56T - 0.265 \times 10^{-3} T^2$$

Since

$$\Delta H_{298} = -22\,500 - (-4800) = -17\,700 \text{ cal/mol}$$

then

$$\begin{aligned} \Delta H_0 &= -17\,700 - 4.56 \times 298.2 + 0.265 \times 10^{-3} \times 298.2^2 = \\ &= -19\,040 \text{ cal/mol} \end{aligned}$$

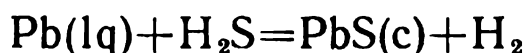
Consequently, for the reaction of hydrogen sulphide with crystalline lead

$$\Delta H = -19\,040 + 4.56T - 0.265 \times 10^{-3} T^2$$

At the melting point of lead

$$\begin{aligned} \Delta H_{600.5} &= -19\,040 + 4.56 \times 600.5 - 0.265 \times 10^{-3} \times 600.5^2 = \\ &= -16\,400 \text{ cal/mol} \end{aligned}$$

Consequently, for the reaction



in accordance with Hess's law

$$\Delta H_{600.5} = -16\,400 + (-1224) = -17\,620 \text{ cal/mol}$$

For this reaction

$$\begin{aligned} \Delta C_p &= 3.48 + 1.55 \times 10^{-3} T \\ \Delta H &= \Delta H_0 + 3.48T + 0.775 \times 10^{-3} T^2 \end{aligned}$$

according to the value of $\Delta H_{600.5} = -17\,620$, we find

$$\Delta H_0 = -19\,990 \text{ cal/mol}$$

Hence for the reaction of hydrogen sulphide with molten lead

$$\Delta H = -19\,900 + 3.48T + 0.775 \times 10^{-3} T^2$$

whence

$$\Delta H_{1223} = -14\,570 \text{ cal/mol}$$

The result of the calculation should be acknowledged as lowered (in absolute value), since the heat of solution of lead sulphide in molten lead was not taken into account in the calculations.

Problems

1. The heat of vaporization of water at $t_1 = 30^\circ\text{C}$ is 580.4 kcal/kg, and at $t_2 = 20^\circ\text{C}$ is 586.0 kcal/kg. Using Eq. (2.21), assess the approximate value of the heat capacity of water vapour in the temperature interval of $t = 30\text{--}35$ if $(C_p)_{\text{H}_2\text{O}}^{\text{lg}} = 18.02 \text{ cal/mol} \cdot \text{K}$.

Compare the result with the accurate value of $(C_p)_{\text{H}_2\text{O}}^g = 8.095$.

2. The temperature dependence of the heat of formation of mercuric sulphide within the interval from 0 to 98 °C is expressed by the equation

$$\Delta H = -10\,393 - 4.627T + 15.9 \times 10^{-3}T^2 - 18.49 \times 10^{-6}T^3$$

Find: (1) the temperature dependence of ΔC_p ;

(2) $(C_p)_{\text{Hg}}$ at $t = 50^\circ\text{C}$ if at this temperature the heat capacities of rhombic sulphur and mercuric sulphide are respectively 5.60 and 12.0 cal/mol·K.

Compare the results of the calculations with the experimental value equal to 6.52 cal/mol·K.

3. The temperature dependence of the molar heat capacity for methane, water vapour (steam), carbon monoxide and hydrogen is expressed by the following data:

T, K	900	1100	1300	1500
$(C_p)_{\text{CH}_4}$	16.21	18.09	19.57	20.71
$(C_p)_{\text{H}_2\text{O}}^g$	9.559	10.172	10.479	11.263
$(C_p)_{\text{CO}}$	7.787	8.058	8.265	8.419
$(C_p)_{\text{H}_2}$	7.139	7.308	7.505	7.713

Find the temperature at which ΔH of the reaction of conversion of the methane into carbon monoxide and hydrogen does not depend on the temperature.

4. The following empirical equations were proposed on the basis of experimental data on the temperature dependence of C_p :

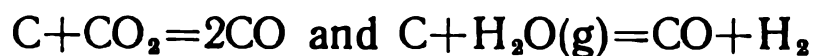
$$(C_p)_{\text{C}_2\text{H}_6} = 1.62 + 42.1 \times 10^{-3}T - 139.0 \times 10^{-7}T^2$$

$$(C_p)_{\text{C}_2\text{H}_4} = 2.08 + 31.1 \times 10^{-3}T - 106.6 \times 10^{-7}T^2$$

$$(C_p)_{\text{H}_2} = 6.956 + 0.97 \times 10^{-3}T$$

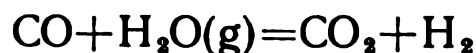
Does the heat of the reaction of hydrogenation of ethylene within the interval of $T = 300$ to 1000 K grow or diminish? Does the rate of its change with a growth in the temperature increase or decrease?

5. For the reactions



the values of ΔH_{500} are respectively 41 501 and 31 981 cal/mol.

Find ΔH_{1000} for the reaction



if

$$(C_p)_{\text{CO}} = 6.60 + 1.20 \times 10^{-3}T$$

$$(C_p)_{\text{H}_2\text{O}}^g = 8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2$$

$$(C_p)_{\text{CO}_2} = 6.25 + 2.09 \times 10^{-3}T - 0.459 \times 10^{-6}T^2$$

$$(C_p)_{\text{H}_2} = 6.62 + 0.81 \times 10^{-3}T$$

6. The heat capacities of carbon, chlorine and phosgene are respectively

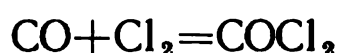
$$(C_p)_{\text{CO}} = 6.79 + 0.98 \times 10^{-3}T - \frac{0.11 \times 10^5}{T^2}$$

$$(C_p)_{\text{Cl}_2} = 8.82 + 0.06 \times 10^{-3}T - \frac{0.68 \times 10^5}{T^2}$$

$$(C_p)_{\text{COCl}_2} = 13.61 + 3.46 \times 10^{-3}T - \frac{1.91 \times 10^5}{T^2}$$

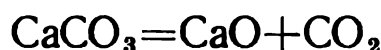
The standard heats of formation of carbon monoxide and phosgene are respectively $-26\,416$ and $-53\,300$ cal/mol.

Find $(Q_V)_{600}$ of the reaction



considering the reactants to be ideal gases.

7. The heat of dissociation of calcium carbonate



at $T=298$ K is $42\,500$ cal/mol.

The heat capacities of the reactants are

$$(C_p)_{\text{CaCO}_3} = 19.68 + 11.89 \times 10^{-3}T - \frac{3.076 \times 10^5}{T^2}$$

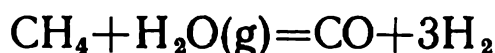
$$(C_p)_{\text{CaO}} = 11.87 + 0.767 \times 10^{-3}T - \frac{1.646 \times 10^5}{T^2}$$

$$(C_p)_{\text{CO}_2} = 10.34 + 2.74 \times 10^{-3}T - \frac{1.955 \times 10^5}{T^2}$$

Find: (1) the equation of $\Delta H=f(T)$;

(2) the consumption of heat for the decomposition of 1 kg of calcium carbonate at $t=1000^\circ\text{C}$.

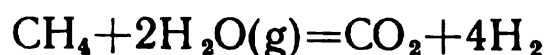
8. The heat of the reaction



at $T=298$ K equals $49\,271$ cal. Find ΔH_{1000} graphically, if the temperature dependence of the heat capacity of the reactants (cal/mol·K) is expressed by the following data:

$T, \text{ K}$	298	400	500	600	800	1000	1200
$(C_p)_{\text{CH}_4}$	8.536	9.736	11.139	12.546	15.10	17.21	18.88
$(C_p)_{\text{H}_2\text{O}}^{\text{g}}$	8.025	8.185	8.415	8.677	9.254	9.869	10.468
$(C_p)_{\text{CO}}$	6.965	7.013	7.120	7.276	7.624	7.932	8.167
$(C_p)_{\text{H}_2}$	6.892	6.974	6.993	7.008	7.078	7.217	7.404

9. Find the equation of $\Delta H=f(T)$ and compute ΔH_{1000} for the reaction



if

$$\Delta H_{298} = 39\,433 \text{ cal/mol}$$

and

$$(C_p)_{\text{CH}_4} = 5.65 + 11.44 \times 10^{-3}T - \frac{0.46 \times 10^5}{T^2}$$

$$(C_p)_{\text{H}_2\text{O}}^g = 7.17 + 2.58 \times 10^{-3}T + \frac{0.08 \times 10^5}{T^2}$$

$$(C_p)_{\text{CO}_2} = 10.55 + 2.16 \times 10^{-3}T - \frac{2.04 \times 10^5}{T^2}$$

$$(C_p)_{\text{H}_2} = 6.52 + 0.78 \times 10^{-3}T + \frac{0.12 \times 10^5}{T^2}$$

Calculate ΔH_{1000} using:

(a) the accurate equation of $\Delta H=f(T)$; (b) the mean values of C_p within the interval of $T=273.2$ to 1000 K (Appendix 6); (c) the values of $(C_p)_{298}$ given below:

Gas	CH ₄	H ₂ O	CO ₂	H ₂
$(C_p)_{298}$, cal/mol·K	8.536	8.025	8.874	6.892

Assess the accuracy of the results of the calculations if the error of the equations of $C_p=f(T)$ averages 0.8% , and the precise value of $\Delta H_{1000}=45590$ cal/mol.

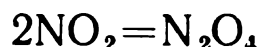
10. The temperature dependence of the enthalpy of nitrogen dioxide and nitrogen tetroxide is expressed by the following equations:

$$(H_T - H_{298})_{\text{NO}_2} = 10.62T + 1.02 \times 10^{-3}T^2 + \frac{1.61 \times 10^5}{T} - 3690$$

and

$$(H_T - H_{298})_{\text{N}_2\text{O}_4} = 20.05T + 4.75 \times 10^{-3}T^2 + \frac{3.56 \times 10^5}{T} - 7594$$

Find ΔH_{400} for the reaction



if $(\Delta H_{298})_{\text{NO}_2}=8030$ and $(\Delta H_{298})_{\text{N}_2\text{O}_4}=3060$ cal/mol.

Chapter Three

THE SECOND LAW OF THERMODYNAMICS

3.1. ENTROPY

Entropy is a function of state of a system whose differential is determined by the equation

$$dS \equiv \frac{\delta Q}{T} \quad (3.1)$$

where δQ is an infinitely small amount of heat supplied to the system in a *reversible* process.

By combining Eq. (3.1) with the differential equations expressing the first law of thermodynamics, we get (at $\delta W' = 0$), respectively

$$dU = T dS - p dV \quad (3.2)$$

and

$$dH = T dS + V dp \quad (3.3)$$

For the relationship $S = f(V, T)$ Eq. (3.2) becomes

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV \quad (3.4)$$

with variable p and T

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_p dp \quad (3.5)$$

with variable p and V

$$dS = \frac{C_V}{T} \left(\frac{\partial T}{\partial p} \right)_V dp + \frac{C_p}{T} \left(\frac{\partial T}{\partial V} \right)_p dV \quad (3.6)$$

Equations (3.2-3.6) can be used to derive a number of expressions relating different properties of a system in a reversible process.

If the condition of constancy of p , V or T is observed, then Eqs. (3.4-3.6) transform into relationships expressing the dependence of S on one parameter. Thus, it follows from Eq. (3.4) that

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad (3.7)$$

and

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (3.8)$$

while from Eq. (3.5) we have

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad (3.9)$$

and

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (3.10)$$

Depending on the properties of the system which general equations (3.4-3.6) are applied to, they acquire the relevant form. Thus, for an ideal gas in accordance with the Mendelev-Clapeyron equation they respectively transform into the equations

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V} \quad (3.11)$$

$$dS = C_p \frac{dT}{T} - R \frac{dp}{p} \quad (3.12)$$

$$dS = C_v \frac{dp}{p} + C_p \frac{dV}{V} \quad (3.13)$$

Integration of Eqs. (3.4-3.13) in accordance with the equation

$$\int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \quad (3.14)$$

ensuing from Eq. (3.1) gives a finite change in the entropy upon a reversible transition from state 1 to state 2. Thus, in a reversible isothermal process (for example, in melting, vaporization, sublimation, allotropic transformations) we have

$$S_2 - S_1 = \frac{Q}{T} \quad (3.15)$$

where S_2 and S_1 = molar (or unit) entropies of the forming and the initial phases

Q and T = heat (molar or respectively unit) and temperature in a given phase transition.

If, for example, a reversible adiabatic process proceeds, then

$$\Delta S = 0 \quad (3.16)$$

In the general case, the object being studied is related by heat exchange with one or more other bodies. Imagine that the part of the latter is played by a reservoir; let us call it the *heat source*. If it is assumed that it is very great or, which is the same, that it has an enormous heat capacity, then its temperature in the process of heat exchange can be considered constant.

Let us extend the boundaries of the system and include a heat source in it in addition to the "working" system (this name will be applied

to the system which a process being studied proceeds in). Now heat exchange will occur within an artificially constructed system, i.e. the latter will be isolated. For this reason in accordance with Eq. (3.16) for the system as a whole we have

$$\Delta S = \Delta S_{\text{work. syst.}} + \Delta S_{\text{heat source}} = 0 \quad (3.17)$$

This means that *when a reversible process proceeds in any isolated system its entropy does not change.*

If an *irreversible* change occurs in a system, then in Eqs. (3.1-3.16) the equality sign must be changed to the sign $>$; thus, for an irreversible isothermal process

$$\Delta S > \frac{Q}{T} \quad (3.18)$$

for an irreversible adiabatic process

$$\Delta S > 0 \quad (3.19)$$

Consequently, applying the above reasoning to irreversible processes, in accordance with Eq. (3.19) we get for a system as a whole

$$\Delta S = \Delta S_{\text{work. syst.}} + \Delta S_{\text{heat source}} > 0 \quad (3.20)$$

i.e. when an irreversible process proceeds in an isolated system, its entropy grows.

The change in the entropy at the given initial and final states of a system does not depend on the path of a process and, in particular, on whether it proceeds reversibly or irreversibly. Only for a reversible process, however, is ΔS related to the characteristics of the process by the equality sign. For this reason for computing ΔS for an irreversible process, it is necessary to mentally conduct it in the reverse direction.

For the calculation of the absolute values of the entropy see Sec. 9.2.

Examples

1. Use Eqs. (3.2) and (3.4) to show that

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{p - T(\partial p/\partial T)_V}{C_V}$$

Solution. It follows from Eqs. (3.2) and (3.4) that

$$T dS = dU + p dV \text{ and } T dS = C_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$$

Hence

$$dU = C_V dT + \left[T \left(\frac{\partial p}{\partial T}\right)_V - p \right] dV$$

whence at $U=\text{const}$

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{p - T(\partial p/\partial T)_V}{C_V}$$

2. Show that isochors will be steeper than isobars in a T - S diagram.

Solution. Assume that an isochor and an isobar have been plotted through a given point in a T - S diagram. The slope of these curves will respectively equal $(\partial T/\partial S)_V$ and $(\partial T/\partial S)_p$. Since $C_p > C_V$, then in accordance with Eqs. (3.7) and (3.9)

$$\left(\frac{\partial T}{\partial S}\right)_V > \left(\frac{\partial T}{\partial S}\right)_p$$

i.e. an isochor will be steeper than an isobar.

3. Show that at $T=\text{const}$ the volume dependence of the isochoric heat capacity is expressed by the equation

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

Solution. Differentiation of Eq. (3.8) with respect to T at $V=\text{const}$ yields

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right]_V = \frac{\partial}{\partial T} \left(\frac{\partial p}{\partial T}\right)_V$$

or

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right]_T = \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

or in accordance with Eq. (3.7)

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

This equation can also be obtained directly from Eq. (3.4). Since dS is a total differential, then

$$\left[\frac{\partial}{\partial V} \left(\frac{C_V}{T}\right)\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial p}{\partial T}\right)_V\right]_V$$

which corresponds to the equation sought.

4. Show with the aid of Eqs. (3.7) and (3.8) that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{Tp}{C_V} \gamma$$

where γ is an isochoric pressure coefficient equal to

$$\gamma = \frac{1}{p} \left(\frac{\partial p}{\partial T}\right)_V$$

Solution. For the relationship $f(T, V, S)=0$ we have

$$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$$

or in accordance with Eqs. (3.7) and (3.8)

$$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial T}{\partial p}\right)_V \frac{C_V}{T} = -1$$

whence

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V} \left(\frac{\partial p}{\partial T}\right)_V = -\frac{T p}{C_V} \frac{1}{p} \left(\frac{\partial p}{\partial T}\right)_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T p}{C_V} \gamma$$

5. Calculate the change in the entropy in the vaporization of one mole of ethyl chloride at $t=12.3^\circ\text{C}$ if $\Delta H_{\text{vap}}=90.0$ cal/g.

Solution. Since vaporization is a reversible isothermal isobaric process, then in accordance with Eq. (3.15) we have

$$\Delta S = S_{\text{C}_2\text{H}_5\text{Cl}}^g - S_{\text{C}_2\text{H}_5\text{Cl}}^{\text{liq}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

or

$$\Delta S = \frac{90.0 \times 64.51}{12.3 + 273.2} = 20.34 \text{ cal/mol} \cdot \text{K}$$

6. The temperature dependence of the density of antimony trichloride (in g/cm^3) within the interval of $t=75$ to 150°C is expressed by the equation

$$\rho = 2.8131 - 0.001636t - 0.0000032t^2$$

Find the change in the entropy of one mole of antimony trichloride per unit of pressure at $t=100^\circ\text{C}$.

Solution. By Eq. (3.10)

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

and, in turn,

$$\frac{\partial V}{\partial T} = -\frac{1}{\rho^2} \frac{\partial \rho}{\partial T}$$

We find

$$\left(\frac{\partial \rho}{\partial t}\right)_p = -0.001636 - 0.0000064t$$

$$\left(\frac{\partial \rho}{\partial t}\right)_{t=100} = -0.001636 - 0.0000064 \times 100 = -0.002276 \text{ g/cm}^3 \cdot \text{K}$$

and

$$\rho_{t=100} = 2.6175 \text{ g/cm}^3$$

Hence

$$\begin{aligned}\left(\frac{\partial V}{\partial T}\right)_{t=100} &= \frac{0.002\,276}{2.6175^2} = 0.000\,332\,3 \text{ cm}^3/\text{g} \cdot \text{K} = \\ &= 228.13 \times 0.000\,332\,3 \text{ cm}^3/\text{mol} \cdot \text{K} = 0.075\,81 \text{ cm}^3/\text{mol} \cdot \text{K}\end{aligned}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_{t=100} = -0.075\,81 \text{ cm}^3/\text{mol} \cdot \text{K} = -0.001\,836 \text{ cal/mol} \cdot \text{K} \cdot \text{atm}$$

7. The molar heat capacity of potassium bromide within the interval of $T=293$ to 923 K is expressed by the equation

$$(C_p)_{\text{KBr}} = 11.56 + 3.32 \times 10^{-3}T$$

Find the change in the entropy of one mole of KBr upon its reversible heating from $T_1=298.2$ to $T_2=500$ K.

Solution. In accordance with Eq. (3.9) we have

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

whence

$$\begin{aligned}S_{500} - S_{298} &= \int_{298}^{500} (11.56 + 3.32 \times 10^{-3}T) \frac{dT}{T} = \\ &= 11.56 \times 2.303 \log \frac{500}{298.2} + 3.32 \times 10^{-3} \times (500 - 298.2) = \\ &= 6.65 \text{ cal/mol} \cdot \text{K}\end{aligned}$$

8. Find the change in the entropy in the process of reversible isothermal compression of: (1) one mole of oxygen from $p_1=0.001$ to $p_2=0.01$ atm and (2) one mole of methane from $p_1=0.1$ to $p_2=1$ atm. Consider the gases to be ideal ones in both cases.

Solution. In accordance with Eq. (3.12) for reversible isothermal compression, we have

$$\Delta S = R \ln \frac{p_1}{p_2} = 4.576 \log \frac{0.001}{0.01} = -4.576$$

and

$$\Delta S = R \ln \frac{p_1}{p_2} = 4.576 \log \frac{0.1}{1.0} = -4.576$$

Coincidence of the results of the calculations is to be expected, since the change in the entropy of ideal gases does not depend on their chemical nature and is determined only by the ratio of the pressures.

9. One of two vessels having the same capacity (30 dm³ each) contains 28 g of nitrogen, and the other 32 g of oxygen. The temperature and pressure are the same in both vessels.

Find the change in the entropy in diffusion appearing as a result of the contents of the two vessels coming into contact. Consider that nitrogen and oxygen are ideal gases.

Solution. The process of diffusion is irreversible. For this reason to calculate ΔS we mentally conduct it in the reverse direction. Owing to the isothermal nature of the process, in accordance with Eq. (3.11) we get

$$\Delta S = nR_1 \ln \frac{V}{V_1} + nR_2 \ln \frac{V}{V_2} = 4.576 (1 \times \log 2 + 1 \times \log 2) = 2.754 \text{ cal/mol} \cdot \text{K}$$

10. In the process of isothermal expansion of an ideal gas, Q calories of heat are supplied from a heat source. The gas expands irreversibly, performing 10% of the maximum work.

Find the change of entropy in the system gas-heat source.

Solution. If the expansion were reversible, i.e. the maximum work were performed, then the entropy of the gas would change in accordance with Eq. (3.15) by $10Q/T$. Owing to the change in the entropy not depending on the path of the process, it will also change by this amount in actual, i.e. irreversible, expansion. Thus for the system as a whole

$$\Delta S = \frac{10Q}{T} + \left(-\frac{Q}{T} \right) = \frac{9Q}{T}$$

Attention should be given to the circumstance that if 20% of the maximum work were performed in expansion, then for an isolated system

$$\Delta S = \frac{5Q}{T} + \left(-\frac{Q}{T} \right) = \frac{4Q}{T}$$

When $W = 0.5W_{\max}$, we have

$$\Delta S = \frac{2Q}{T} + \left(-\frac{Q}{T} \right) = \frac{Q}{T}$$

Finally in the limiting case, when $W = W_{\max}$ (i.e. if the process were reversible)

$$\Delta S = \frac{Q}{T} + \left(-\frac{Q}{T} \right) = 0$$

Thus, this example is an excellent illustration of the fact that entropy is a measure of the irreversibility of a process.

11. Find the change in the entropy when 100 calories of heat pass from a body with a temperature of 150°C to one with a temperature of 50°C .

Solution. The process of heat transfer is irreversible; to calculate ΔS it must be conducted in the reverse direction. For this purpose we conduct it in a reversible Carnot cycle in which the heat source will

have a temperature of 150 °C, and the heat sink (receiver) one of 50 °C. The change in the entropy for the heat source will be

$$\frac{-100}{423.2} = -0.2363 \text{ cal/mol} \cdot \text{K}$$

and for the heat sink

$$\frac{+100}{323.2} = +0.3094 \text{ cal/mol} \cdot \text{K}$$

Consequently,

$$\Delta S = 0.3094 + (-0.2363) = 0.0731 \text{ cal/mol} \cdot \text{K}$$

The calculation can also be performed in a different way. Assume that the 100 calories transferred from the source to the sink are returned with the aid of a reversible Carnot cycle. In this case the entropy in the source and the sink will change by

$$\frac{100}{323.2} = 0.3094 \text{ cal/mol} \cdot \text{K}$$

But the sink receives the work done externally together with the 100 calories of heat. Since

$$Q_1 = Q_2 \frac{T_2}{T_1} = 100 \times \frac{423.2}{323.2} = 130.94$$

then in the given process the sink will receive 130.94—100=30.94 cal of heat. Hence

$$\Delta S = \frac{30.94}{423.2} = 0.0731 \text{ cal/mol} \cdot \text{K}$$

12. A long vertical tube is filled with a gas. Find the relation between the pressure at the bottom of the tube and at a height h if the gas is ideal, its temperature is T and its molecular weight is M .

Solution. Assume that one mole of the gas is lowered from a height h to $h=0$ and its pressure changes from p to p_0 with its temperature remaining constant (since the gas is ideal). For this reason if the process is reversible, then in accordance with Eq. (3.12) the change in the entropy of the gas will be

$$\Delta S_g = R \ln \frac{p}{p_0}$$

The work performed, equal to the potential energy of one mole of the gas at the height h (with respect to $h=0$)

$$W = Mgh$$

where g is the acceleration of gravity, will be transferred in the form

of heat to the heat source whose entropy will change by

$$\Delta S_{\text{heat source}} = \frac{Mgh}{T}$$

Since the system is an adiabatic one, then according to Eq. (3.17)

$$R \ln \frac{p}{p_0} + \frac{Mgh}{T} = 0 \quad \text{or} \quad p = p_0 e^{-\frac{Mgh}{RT}}$$

13. Find the change in the entropy in the process of solidification of supercooled benzene at $t = -5^\circ\text{C}$ if at $t = 5^\circ\text{C}$ we have

$$(\Delta H_{\text{fus}})_{\text{C}_6\text{H}_6} = 2370 \text{ cal/mol}$$

$$(C_p)_{\text{C}_6\text{H}_6}^{\text{liq}} = 30.3 \text{ cal/mol} \cdot \text{K}$$

and

$$(C_p)_{\text{C}_6\text{H}_6}^{\text{c}} = 29.3 \text{ cal/mol} \cdot \text{K}$$

Solution. The value of $(\Delta H_{\text{fus}})_{\text{C}_6\text{H}_6}$ at $t = -5^\circ\text{C}$ can be found approximately by Eq. (2.25)

$$\Delta H_{268} \approx \Delta H_{278} + [(C_p)_{\text{C}_6\text{H}_6}^{\text{c}} - (C_p)_{\text{C}_6\text{H}_6}^{\text{liq}}] \times (268.2 - 278.2)$$

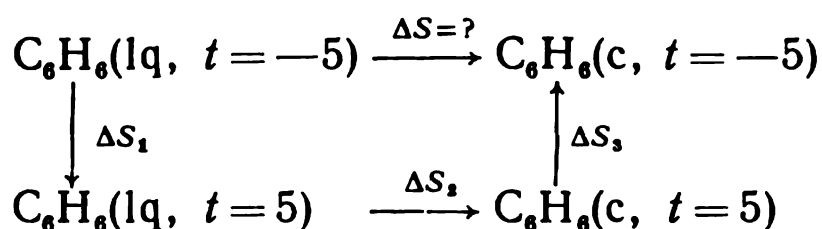
whence

$$\Delta H_{268} = -2370 + (29.3 - 30.3)(-10) = -2360 \text{ cal/mol}$$

Since the process is irreversible, then

$$\Delta S > -\frac{2360}{268.2}$$

To find ΔS , let us mentally conduct the process reversibly in three steps:



obviously,

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

consequently in accordance with Eqs. (3.9) and (3.15) we have

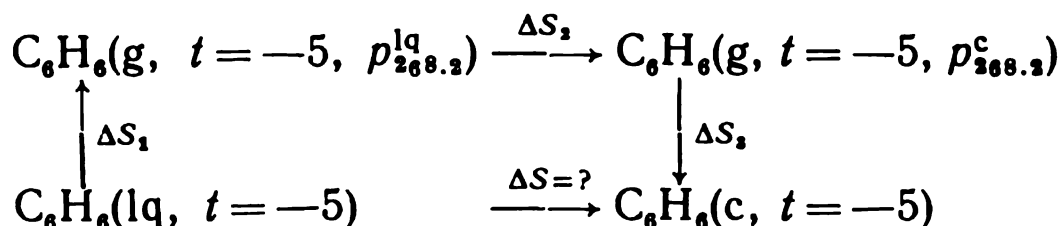
$$\Delta S = \int_{268.2}^{278.2} 30.3 \frac{dT}{T} + \frac{(\Delta H_s)_{\text{C}_6\text{H}_6}}{278.2} + \int_{278.2}^{268.2} 29.3 \frac{dT}{T} = -8.48$$

(For the system benzene + heat source we have $\Delta S = -8.48 + \frac{2360}{268.2} = 0.31 \text{ cal/mol} \cdot \text{K}$.)

14. Using the value of ΔS found in solving Example 13, determine the pressure of the saturated vapour over supercooled liquid benzene at $t = -5^\circ\text{C}$ if $p_{\text{C}_6\text{H}_6}^c$ at $t = -5^\circ\text{C}$ is approximately equal to 17.1 mm Hg. Compare the results of the calculation with the value found by the equation

$$\log p \text{ (mm Hg)} = 7.0664 - \frac{1298}{230 + t}$$

Solution. We mentally conduct the process of solidification of the benzene through the vapourous phase reversibly:



where $p_{268.2}^{\text{lg}}$ and $p_{268.2}^c$ are the pressures of the saturated vapour at $t = -5^\circ\text{C}$ over the supercooled liquid and crystalline benzene, respectively.

Obviously

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

or, according to Eqs. (3.15) and (3.12):

$$\begin{aligned} \Delta S &= \frac{(\Delta H_{\text{vap}})_{\text{C}_6\text{H}_6}}{268.2} + \left(-R \ln \frac{p_{268.2}^c}{p_{268.2}^{\text{lg}}} \right) + \frac{(\Delta H_{\text{desubl}})_{\text{C}_6\text{H}_6}}{268.2} = \\ &= -R \ln \frac{p_{268.2}^c}{p_{268.2}^{\text{lg}}} + \frac{(\Delta H_s)_{\text{C}_6\text{H}_6}}{268.2} \end{aligned}$$

In accordance with the result obtained in solving Example 13, we have

$$-8.48 = -4.576 \log \frac{17.1}{p_{268.2}^{\text{lg}}} + \frac{-2360}{268.2}$$

or

$$-8.48 = -4.576 \log 17.1 + 4.576 \log p_{268.2}^{\text{lg}} - \frac{2360}{268.2}$$

whence

$$\log p_{268.2}^{\text{lg}} = \frac{-8.48 + 5.641 + 8.799}{4.576} = \frac{5.96}{4.576} = 1.3028$$

i.e.

$$p_{268.2}^{\text{lg}} = 20.08 \text{ mm Hg}$$

According to the equation given in the initial conditions of the present example, we have

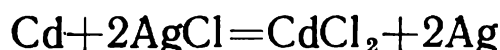
$$\log p_{\text{C}_6\text{H}_6}^{\text{lg}} \text{ (mm Hg)} = 7.0664 - \frac{1298}{230 + (-5)} = 1.2975$$

i.e.

$$p_{\text{C}_6\text{H}_6}^{\text{lg}} = 19.84 \text{ mm Hg}$$

which differs from the found value by 1.2%.

15. Find the change in the entropy as a result of the reaction



if $E = 0.6753 \text{ V}$ corresponds to its being conducted in a galvanic cell at $p = 1 \text{ atm}$ and $t = 25^\circ\text{C}$ in conditions when the e.m.f. of the cell is compensated by an e.m.f. applied externally. The standard heats of formation of cadmium chloride and silver chloride are respectively $-93\,100$ and $-30\,300 \text{ cal/mol}$.

Solution. The heat of the reaction in accordance with Hess's law is

$$\begin{aligned}\Delta H &= (\Delta H_{\text{form}})_{\text{CdCl}_2} - 2(\Delta H_{\text{form}})_{\text{AgCl}} = \\ &= -93\,100 - 2(-30\,300) = -32\,500 \text{ cal/mol}\end{aligned}$$

Since the reaction is irreversible, then

$$\Delta S_{\text{work. syst.}} > \frac{-32\,500}{298.2}$$

To calculate $\Delta S_{\text{work. syst.}}$ it is necessary to conduct the reaction reversibly. The process will be practically reversible in conditions of compensation of the e.m.f. of the cell by a counter electromotive force. By conducting the reaction in a galvanic cell, we would get the work

$$W = zEF$$

where z = valence of a reacting ion

E = e.m.f. of the cell

F = Faraday constant.

In the given case

$$W = 2 \times 0.6753 \times 23\,062 = 31\,150$$

Since ΔH does not depend on the path of the process, it will have the same value in a reversible process. Hence

$$\Delta S_{\text{work. syst.}} = \frac{-32\,500 + 31\,150}{298.2} = -4.527 \text{ cal/mol} \cdot \text{K}$$

i.e. in the process of reaction of the cadmium with the silver chloride the entropy diminishes by $4.52 \text{ cal/mol} \cdot \text{K}$ (regardless of whether the reaction proceeds reversibly or irreversibly).

16. Show that $(\partial T / \partial V)_S = -(\partial p / \partial S)_V$ and with the aid of this equation check the agreement of the data for steam if $p = 92 \text{ kgf/cm}^2$, $t = 401^\circ\text{C}$, $S = 1.500 \text{ cal/kg} \cdot \text{K}$ and $v = 0.03 \text{ m}^3/\text{kg}$.

Use the data in Table 6 for the solution, obtained by linear interpolation in the corresponding reference book.

Table 6

S=1.500 kcal/kg·K			v=0.0300 m³/kg		
v, m³/kg	t, °C	p, kgf/cm²	S, kcal/kg·K	p, kgf/cm²	t, °C
0.037 09	359.5	70	1.4641	82	351.7
0.033 41	379.0	80	1.4791	86	371.1
0.031 58	390.3	86	1.500	92	401.1
0.029 98	401.1	92	1.5213	98	432.3
0.028 54	410.8	98	1.5450	105	469.5
0.026 06	429.1	110			
0.023 55	449.8	125			

Solution. This equation can be obtained from Eq. (3.2) by applying the theorem on the total differential to it.

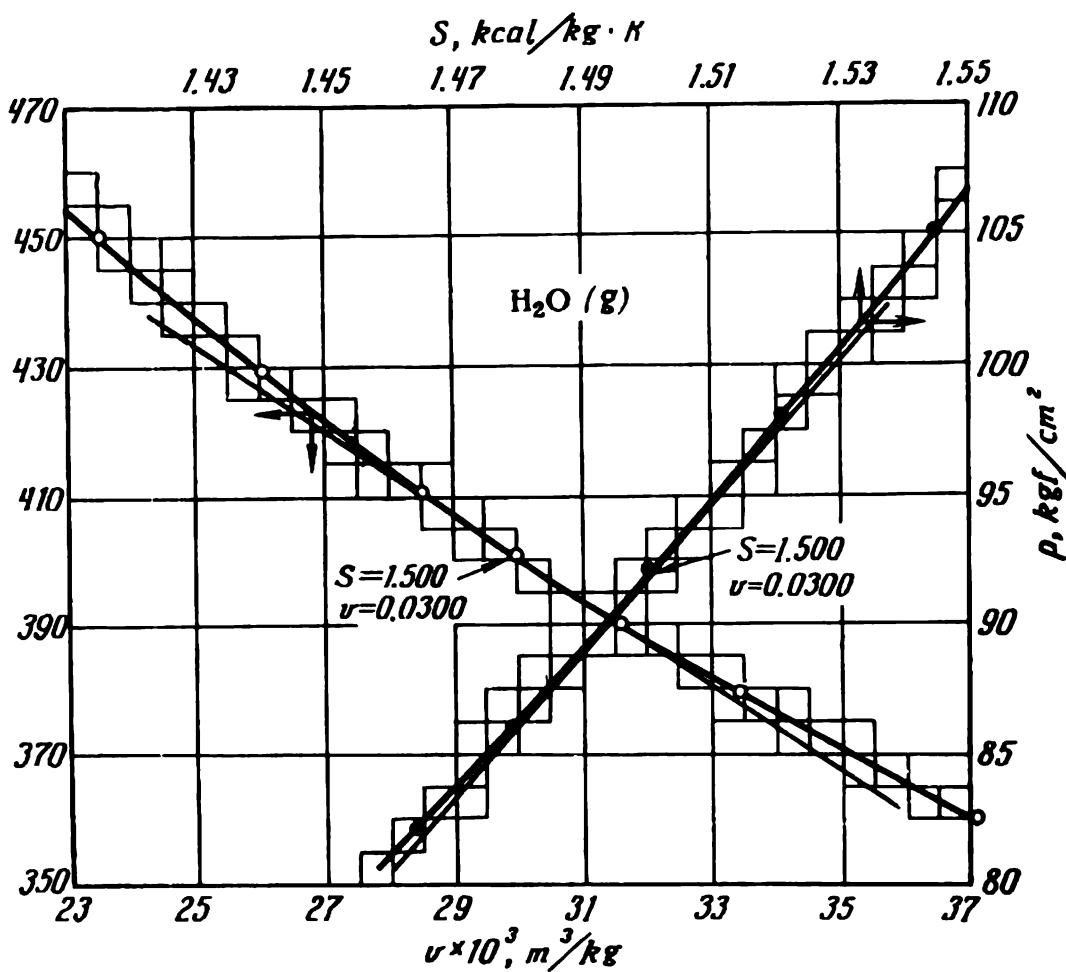


Fig. 6

We use the data in Table 6 to plot a combined chart of t versus v at $S=\text{const}$ and p versus S at $v=\text{const}$ (Fig. 6). Graphical differentiation yields

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{440 - 361}{0.024 - 0.036} = -\frac{79}{0.012} = -6580 \text{ K} \cdot \text{kg/m}^3$$

and

$$\left(\frac{\partial p}{\partial S}\right)_V = \frac{103 - 80.5}{1.540 - 1.460} = \frac{22.5}{0.080} = 281 \text{ K} \cdot \text{kg}^2/\text{cm}^2 \cdot \text{kcal}$$

or

$$\frac{281 \times 1000}{1.033 \times 41.293} = 6590 \text{ K} \cdot \text{kg}/\text{m}^3$$

The discrepancy equal to 0.2% and obviously due to the inaccuracy of the graphical differentiation is within the limits of the error of tabulated data.

Problems

1. Show that

$$\frac{\partial^2 H}{\partial T \partial p} = T \frac{\partial^2 S}{\partial T \partial p}$$

2. Show that

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - p \left(\frac{\partial V}{\partial T}\right)_p$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T$$

3. Show with the aid of Eqs. (3.3), (3.7) and (3.8) that

$$\left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V + V \left(\frac{\partial p}{\partial V}\right)_T$$

and

$$\left(\frac{\partial H}{\partial T}\right)_V = C_V + V \left(\frac{\partial p}{\partial T}\right)_V$$

4. Using the equation derived in Example 2, show that the isochoric heat capacity of an ideal gas upon its isothermal expansion (or compression) does not depend on the volume.

5. Prove the truth of the relationship

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p$$

From the found relationship and the equation

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

obtain the equation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

expressing the dependence of the isobaric heat capacity on the pressure in an isothermal process.

Is it possible to derive the latter equation from Eq. (3.5)?

How will C_p change upon the isothermal compression of an ideal gas?

6. The relationship between C_p and C_v can be expressed by the equation

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

Using the equation

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p$$

obtained from Eqs. (3.2) and (3.8) and the one derived in solving Example 5, show the truth of the following relationships:

$$C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p \quad (a)$$

$$C_p - C_v = \left[V - \left(\frac{\partial H}{\partial p} \right)_T \right] \left(\frac{\partial p}{\partial T} \right)_v \quad (b)$$

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial V} \right)_T \quad (c)$$

$$C_p - C_v = -T \left(\frac{\partial p}{\partial T} \right)_v^2 \left(\frac{\partial V}{\partial p} \right)_T \quad (d)$$

7. Which of the equations derived in solving Example 6 can be directly transformed into the equation

$$C_p - C_v = \frac{\alpha^2 TV}{\kappa}$$

where $\alpha = V^{-1}(\partial V/\partial T)_p$ = cubic expansion coefficient

$\kappa = V^{-1}(\partial V/\partial p)_T$ = isothermal compressibility?

At $t = 0^\circ\text{C}$ find C_p/C_v for liquid chlorobenzene, if for this compound we have $\alpha = 9534 \times 10^{-7}$, $\kappa = 643 \times 10^{-7}$, $(C_p)_{t=0} = 33.63 \text{ cal/mol} \cdot \text{K}$ and $\rho_{\text{C}_6\text{H}_5\text{Cl}}^{\text{liq}} = 1.12782 \text{ g/cm}^3$.

8. Show by means of Eqs. (3.9) and (3.10) that

$$C_p = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_S \quad (a)$$

and on the basis of the results obtained in solving Example 4 that

$$\frac{C_v}{C_p} = \frac{(\partial V/\partial p)_S}{(\partial V/\partial p)_T} \quad (b)$$

9. Show that from formula (a) derived in solving Problem 8 it follows that for an ideal gas

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}}$$

where $\gamma = C_p/C_v$.

10. The density of liquid sulphuric acid (in g/cm³) within the interval from 0 to 76 °C is expressed by the equation

$$\rho^{la} = 1.854 - 0.000\,98t$$

Use Eq. (a) of Problem 8 to find what change in the temperature would accompany an instantaneous rise in the pressure (by 1 atm) at $t=25^\circ\text{C}$ if the temperature dependence of the unit heat capacity of sulphuric acid within the interval from 10 to 45 °C is expressed by the equation

$$\frac{C_p}{M} = 0.339 + 0.000\,38t$$

11. The temperature dependence of the density of water is expressed by the following data:

$t, ^\circ\text{C}$	40	50	60	70	80	90
$\rho, \text{g/cm}^3$	0.9922	0.9881	0.9832	0.9778	0.9718	0.9653

Using Eq. (a) of Problem 8, determine the change in the temperature of water for an adiabatic increase of the pressure from $p_1=1$ to $p_2=100$ atm if $t=65^\circ\text{C}$ (neglect the influence of the pressure on the density).

Find the values of $(\partial V/\partial T)_p$ needed for the calculations by graphical differentiation. (The recommended scale is 1 °C in 3 mm and 0.01 cm³/g in 50 mm.)

12. Determine the change in the entropy in the melting of 1 g-atom of antimony if $t_{\text{fus}}=630^\circ\text{C}$ and $\Delta H_{\text{fus}}=485$ cal/mol.

13. What will the change in the entropy be upon the sublimation of 1 mole of cyclohexane if $(\Delta H_{\text{fus}})_{280}=628$ and $(\Delta H_{\text{vap}})_{298}=7983$ cal/mol? Perform the calculations for the average temperature.

14. Find the growth in the entropy of propane per unit of volume at $t=-47.75^\circ\text{C}$ if the temperature dependence of its saturated vapour pressure is expressed by the equation

$$\log p \text{ (mm Hg)} = 6.856\,58 - \frac{798.456}{248.581 + t}$$

15. Find $(\partial S/\partial T)_p$ for cobalt chloride at $T=500$ K if its molar heat capacity is determined by the equation

$$C_p = 14.41 + 14.60 \times 10^{-3}T$$

16. Find the change in the entropy in heating one gramme of nickel sulphide from 20 to 80 °C if its mean heat capacity within the temperature interval from 15 to 100 °C is approximately 11.33 cal/mol · K.

17. Show that the equation of the isoentropic curve of a gas for which the van der Waals equation of state holds, viz.

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT$$

has the form

$$T(V-b)^{R/C_V} = \text{const}$$

18. Show that if the temperature dependence of C_p is given by Eq. (2.9), then the temperature dependence of S is expressed by the equation

$$S_{T_2} - S_{T_1} = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c'}{2} \left(\frac{1}{T_2^2} - \frac{1}{T_1^2} \right)$$

19. Considering carbon monoxide to be an ideal gas, find its molar entropy at $t=200^\circ\text{C}$ and $p=50$ atm, if its entropy at $t=25^\circ\text{C}$ and $p=1$ atm is 47.32 cal/mol·K, and the temperature dependence of the heat capacity is expressed by the equation

$$C_p = 6.60 + 1.20 \times 10^{-3}T$$

20. Find the change in the entropy when one mole of cadmium sulphide is heated from $t_1=-100$ to $t_2=0^\circ\text{C}$ if the following equation is proposed for the temperature dependence of the heat capacity in the interval from 138 to 299 K:

$$C_p = 3.53 + 5.31 \times 10^{-3}T - 7.0 \times 10^{-5}T^2$$

21. The heat capacity of *o*-chlorotoluene has the following values:

$t, ^\circ\text{C}$	77.7	99.5	118.5	145
$C_p, \text{cal/g}\cdot\text{K}$	0.3503	0.3595	0.3654	0.3756

Find the change in the entropy upon the isobaric heating of one mole of *o*-chlorotoluene from 90 to 130°C .

22. Show that the change in the entropy caused by isobaric elevation of the temperature from 298.2 K to T can be expressed by the equation

$$S_T - S_{298} = \frac{H_T - H_{298}}{T} + \int_{298}^T \frac{H_T - H_{298}}{T^2} dT$$

How can this equation be used to calculate $S_T - S_{298}$ from the temperature dependence of $H_T - H_{298}$?

23. On the basis of the values of the heat capacity of cadmium chloride obtained at a high temperature, the temperature dependence of the molar enthalpy of cadmium chloride is expressed by the following data:

T, K	400	500	600	700	800
$H_T - H_{298}, \text{cal/mol}$	1780	3720	5750	7840	9900

Find the change in the entropy when one mole of this compound is heated from $T_1=298.2$ to $T_2=800$ K.

Use the equation derived in solving the preceding problem for the calculations.

24. Find the change in the entropy when 1 g-atom of cadmium is heated from $t_1=25$ to $t_2=727^\circ\text{C}$ if $t_{\text{fus}}=321^\circ\text{C}$, $\Delta H_{\text{fus}}=1460$ cal/mol, $(C_p)_{\text{Cd}}=5.46+2.466\times 10^{-3}T$ and $(C_p)_{\text{Cd}}^{\text{lg}}=7.13$ cal/mol \cdot K.

25. One mole of an ideal gas occupying a volume of 20 dm³ is subjected to isothermal expansion. What final volume does a change in the entropy equal to 9.15 cal/mol \cdot K correspond to?

26. By how much will the entropy change as a result of isothermal changing of the state of 10 g of krypton if $V_1=50$ dm³, $p_1=1$ atm and $V_2=200$ dm³, $p_2=0.25$ atm? Consider krypton to be an ideal gas.

27. Nitrogen in an amount of 11.2 dm³ is heated from $t_1=0$ to $t_2=50^\circ\text{C}$, the pressure being simultaneously reduced from $p_1=1$ to $p_2=0.01$ atm. Find the change in the entropy if $C_p\approx 7.0$ cal/mol \cdot K. Consider nitrogen to be an ideal gas.

28. Find the change in the entropy upon isothermal ($t_{\text{n.b.p.}}=80^\circ\text{C}$) compression of benzene vapour from $p_1=0.4$ to $p_2=1$ atm with the following condensation and cooling of the liquid benzene to $t=60^\circ\text{C}$, if $(\Delta H_{\text{vap}})_{\text{n.b.p.}}=7380$ cal/mol and $(C_p/M)_{\text{C}_6\text{H}_6}^{\text{lg}}\approx 0.43$ kcal/g \cdot K. Consider the benzene vapour to be an ideal gas.

29. Show that in the isothermal mixing of ideal gases at the pressure p the entropy changes (calculated per mole of the mixture) by the amount

$$-R\sum x_i \ln x_i$$

where x_i is the mole fraction of the i -th component of the mixture.

30. Find the change in the entropy when 1 dm³ of hydrogen is mixed with 0.5 dm³ of methane if the components and the mixture formed are at $t=25^\circ\text{C}$ and $p=0.9$ atm and the laws of ideal gases hold for them.

31. Find the change in the entropy in the process of separation of one mole of an ideal gas mixture into its components (at constant p and T).

32. Find the change in the entropy when one mole of an ideal gas is throttled at $t=25^\circ\text{C}$ from $p_1=5$ to $p_2=1$ atm.

33. Find the change in the entropy in an isolated system upon the isothermal expansion of one mole of an ideal gas from $V_1=50$ to $V_2=100$ dm³ for:

- (1) reversible expansion;
- (2) expansion in a vacuum;
- (3) expansion at which 50% of the maximum possible work is performed.

34. An iron plate with a mass of 10 grammes heated to 200°C is immersed in a vessel containing 1 dm³ of water at 20°C . What is the change in the entropy if $(C_p)_{\text{Fe}}=6.1$ and $(C_p)_{\text{H}_2\text{O}}^{\text{lg}}=18.0$ cal/K?

35. Find the change in the entropy in the process of mixing 5 kg of water at $t_1=80^\circ\text{C}$ with 10 kg of water at $t_2=20^\circ\text{C}$. Assume that the specific heat capacity of water equals unity. Neglect the influence of the temperature on the entropy and heat capacity.

36. There are two heat sources whose temperatures are respectively equal to 400 and 300 K, and whose heat capacities are constant and equal to 25 and 30 cal/mol·K.

1. Find the work done in the reversible levelling out of the temperatures.

2. What would the temperature be if the process proceeded irreversibly?

37. Find the change in the entropy when the contents of two vessels come into contact, one of which contains 0.5 mole of liquid benzene in equilibrium with 0.5 mole of crystalline benzene, and the other 0.8 mole of water and 0.2 mole of ice. The vessels are confined in an adiabatic shell. The data needed for calculations are given in Table 7.

Table 7

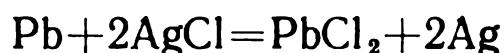
Substance	$t_{\text{fus}}, ^\circ\text{C}$	$C_p^{\text{liq}},$ cal/mol·K	$C_p^{\text{c}},$ cal/mol·K	$\Delta H_{\text{fus}},$ cal/mol
C_6H_6	5.5		29.35	2370
H_2O	0	18.03		1436

38. Find the change in the entropy in the process of condensation of one mole of supercooled water vapour at $p=1$ atm and $t=25^\circ\text{C}$ if $p_{298}=0.032\,29$ kgf/cm², $(\Delta H_{\text{vap}})_{298}=583.2$ kcal/kg, $(\Delta H_{\text{vap}})_{373}=538.9$ kcal/kg, $(C_p)_{\text{H}_2\text{O}}^{\text{g}}=8.025$ and $(C_p)_{\text{H}_2\text{O}}^{\text{liq}}=18.02$ cal/mol·K. Neglect the quantity $(\partial V/\partial T)$ for water. Perform the calculations in two ways.

39. Find the change in the entropy in the process of reversible liquefaction of one mole of methane if $p=1$ atm, the initial temperature is 25°C and the final temperature is $T_{\text{n.b.p.}}$ (111.8 K). The quantities $(\Delta H_{\text{vap}})_{111.8}=1968$ cal/mol and $(C_p)_{\text{CH}_4}=7.8$ cal/mol·K.

Use the results obtained in the solution to calculate the work done in liquefying the methane, assuming the efficiency to equal 10%.

40. Find the change in the entropy in the process



if $E=0.4900$ V corresponds to the conducting of this reaction in a galvanic cell at 25°C , the heats of formation of PbCl_2 and AgCl being respectively equal to $-85\,500$ and $-30\,300$ cal/mol.

What does the entropy of lead at 25°C equal if $S_{\text{AgCl}}=23.0$, $S_{\text{PbCl}_2}=32.6$ and $S_{\text{Ag}}=10.2$ cal/mol·K? Compare the result obtained with the tabulated value (15.49).

Calculate the change in the entropy when this reaction is conducted in an isolated system.

3.2. THERMODYNAMIC POTENTIALS

The thermodynamic potentials include the internal energy U , the enthalpy H , the Helmholtz energy* A and the Gibbs energy** G . A decrease in these functions in an equilibrium process proceeding at constant values of a definite pair of thermodynamic parameters (respectively S and V , S and p , T and V , T and p) is equal to the work done by a system minus the work against the external pressure. The greatest practical use is found by the Helmholtz energy and especially by the Gibbs energy.

The *Helmholtz energy* is determined by the equation

$$A = U - TS \quad (3.21)$$

The decrease in the function A in accordance with the equation

$$\Delta A = \Delta U - T \Delta S \quad (3.22)$$

is equal to the maximum work done by a system provided that a reversible *isothermal process* takes place in it, i.e.

$$-\Delta A = W_{\max} \quad (3.23)$$

If, in particular, a chemical reaction proceeds in a galvanic cell, then

$$-\Delta A = nEF + \int_1^2 p dV \quad (3.24)$$

where n = valence

E = electromotive force

F = Faraday constant.

The relationship between the heat of the corresponding irreversible process and the work of the corresponding reversible process is expressed by the *Gibbs-Helmholtz equations*

$$\Delta A_{V, T} = \Delta U_V + T \left(\frac{\partial \Delta A}{\partial T} \right)_V \quad (3.25) \quad \Delta G_{p, T} = \Delta H_p + T \left(\frac{\partial \Delta G}{\partial T} \right)_p \quad (3.25a)$$

* Other terms used are the isochoric potential, the isothermal potential at constant volume, the isochoric-isothermal potential (free energy, useful energy, work function).

** Other terms used are the isobaric potential, the isobaric-isothermal potential (thermodynamic potential, free enthalpy).

An elementary change in the functions being considered is determined by the corresponding equations

$$dA = -p dV - S dT \quad (3.26)$$

$$dG = V dp - S dT \quad (3.26a)$$

In an irreversible process proceeding at T , $V = \text{const}$, the Helmholtz energy diminishes, and at the moment when equilibrium is reached becomes minimum; in a reversible isochoric-isothermal process it does not change.

In an irreversible process proceeding at T , $p = \text{const}$, the Gibbs energy diminishes, and at the moment when equilibrium is reached becomes minimum; in a reversible isobaric-isothermal process it does not change.

All possible cases are covered by the relationships

$$dA_{V, T} \leq 0 \text{ and } \Delta A_{V, T} \leq 0 \quad (3.27) \quad dG_{p, T} \leq 0 \text{ and } \Delta G_{p, T} \leq 0 \quad (3.27a)$$

The thermodynamic functions are simultaneously *characteristic functions*, i.e. such functions of the state of a system through which and (or) through whose derivatives (of different orders) the thermodynamic properties of a system can be explicitly expressed, namely, $U = f(V, S)$; $H = f_1(p, S)$, $A = f_2(V, T)$ and $G = f_3(p, T)$.

Examples

1. What sign will the quantity ΔG have for the processes:

(1) $\text{C}_6\text{H}_6(\text{lq}, t=0^\circ\text{C}) = \text{C}_6\text{H}_6(\text{c}, t=0^\circ\text{C})$

(2) $\text{C}_6\text{H}_6(\text{lq}, t=5.5^\circ\text{C}) = \text{C}_6\text{H}_6(\text{c}, t=5.5^\circ\text{C})$ and

(3) $\text{C}_6\text{H}_6(\text{lq}, t=10^\circ\text{C}) = \text{C}_6\text{H}_6(\text{c}, t=10^\circ\text{C})$

if $t_{\text{fus}} = 5.5^\circ\text{C}$?

Solution. Since at $t=0$ and $t=10^\circ\text{C}$ the liquid and crystalline benzene are not in equilibrium, ΔG_1 and ΔG_3 will not be equal to zero, while ΔG_2 ($t=5.5^\circ\text{C}$) will be equal to zero.

In the first case $\Delta G_1 = \int_{273.2}^{278.7} -S_{\text{C}_6\text{H}_6}^{\text{lq}} dT + 0 + \int_{278.7}^{273.2} -S_{\text{C}_6\text{H}_6}^{\text{c}} dT$ since $S_{\text{C}_6\text{H}_6}^{\text{lq}} > S_{\text{C}_6\text{H}_6}^{\text{c}}$, then $\Delta G_1 < 0$, i.e. the crystalline benzene will be the stable phase.

In the third case $\Delta G_3 = \int_{283.2}^{278.7} -S_{\text{C}_6\text{H}_6}^{\text{lq}} dT + 0 + \int_{278.7}^{283.2} -S_{\text{C}_6\text{H}_6}^{\text{c}} dT > 0$, i.e. the liquid benzene will be the stable phase.

2. At -5°C , the pressure of the saturated vapour over crystalline benzene is 17.1 mm Hg, and over supercooled liquid benzene is 19.8 mm.

Find the change in the Gibbs energy in the process of solidification of one mole of supercooled benzene at the indicated temperature. Consider the benzene vapour to be an ideal gas.

Solution. Let us mentally conduct the process in three steps, namely, (1) reversible evaporation of the benzene, (2) expansion of the vapour to the equilibrium pressure over the crystalline phase, and (3) condensation of it into the crystalline phase. Hence

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$$

Since the first and the third steps at p , $T = \text{const}$ proceed reversibly, then

$$\Delta G_1 = 0 \text{ and } \Delta G_3 = 0$$

But in accordance with Eq. (3.26a) ΔG_2 is determined by the quantity

$$\int_1^2 V dp = \int_{p_1}^{p_2} \frac{RT}{p} dp$$

consequently,

$$\Delta G = 4.576 \times 268.2 \log \frac{17.1}{19.8} = -78.1 \text{ cal/mol}$$

The result shows the irreversible nature of the considered process.

3. Find Q , W , ΔU , ΔS , ΔH , ΔA and ΔG in the process of reversible vaporization of one mole of water at $p = 0.15 \text{ kgf/cm}^2$. Use the following data for the calculations: $t_b = 53.6^\circ\text{C}$, $V^g = 10.21 \text{ m}^3/\text{kg}$, $V^{lq} = 0.0010137 \text{ m}^3/\text{kg}$ and $\Delta H_{\text{vap}} = 567.0 \text{ kcal/kg}$.

Solution:

$$Q = 567.0 \times 18.016 = 10\,215 \text{ cal/mol}$$

$$W = p(V^g - V^{lq}) = \frac{0.15 \times 10^4 (10.21 - 0.001\,01) \times 18.016}{426.9} = 646 \text{ cal}$$

$$\Delta U = Q - W = 10\,215 - 646 = 9\,569 \text{ cal/mol}$$

$$\Delta H = Q = 10\,215 \text{ cal/mol}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{10\,215}{53.6 + 273.2} = 31.26 \text{ cal/mol} \cdot \text{K}$$

$$\Delta A = -W = -646 \text{ cal/mol}$$

$$\Delta G = 0$$

4. Show that for an ideal gas

$$\left(\frac{\partial A}{\partial T}\right)_p = -S - R \quad (1) \quad \text{and} \quad \left(\frac{\partial A}{\partial p}\right)_T = -V \quad (2)$$

Solution. Since at variable p and T the characteristic function is G , we shall use Eq. (3.21a). Combining it with Eqs. (3.21) and (1.2), we get

$$A = G - pV$$

It follows from this equation that

$$\left(\frac{\partial A}{\partial T}\right)_p = \left(\frac{\partial G}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial T}\right)_p \quad (1)$$

or in accordance with the Mendelev-Clapeyron equation and Eq. (3.26a) we have

$$\left(\frac{\partial A}{\partial T}\right)_p = -S - p \frac{R}{p} = -S - R$$

From the same equation we have

$$\left(\frac{\partial A}{\partial p}\right)_T = \left(\frac{\partial G}{\partial p}\right)_T - p \left(\frac{\partial V}{\partial p}\right)_T - V \quad (2)$$

or in accordance with the Mendelev-Clapeyron equation and Eq. (3.26a) we have

$$\left(\frac{\partial A}{\partial p}\right)_T = V - V - V = -V$$

Problems

1. Show that the decrease in the Helmholtz energy is equal to the entropy with a growth in the temperature at constant volume, and the decrease in this energy is equal to the pressure with a growth in the volume at constant temperature.

2. Show that

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p$$

3. What is the derivative of the change in the Gibbs energy with respect to the pressure at $T=\text{const}$?

What is the physical meaning of this quantity?

4. What form will Eqs. (3.26) and (3.26a) acquire for an ideal gas?

5. On the basis of the solution of Problem 4, find the difference between ΔA and ΔG for an ideal gas and an isothermal process.

6. For calculating the compressibility of a liquid at $T=\text{const}$, we can use the *Byron formula*

$$\frac{V}{M} = A + \frac{B}{C + p}$$

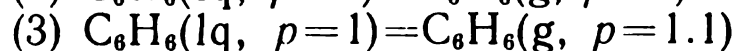
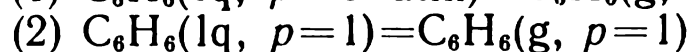
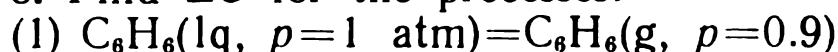
where A , B and C are coefficients which may be considered to depend only on the temperature with a small interval of pressures.

Find: (1) an equation showing how p affects G ;

(2) the change in the Gibbs energy upon the compression of 1 kg of ethyl alcohol from 1 to 500 atm if for this compound up to a pressure of 1000 to 1300 atm we have $A=0.7598$, $B=425.89$ and $C=1779.3$.

7. Find ΔG upon the compression of 1 mole of liquid carbon tetrachloride from $p_1=1$ to $p_2=10$ atm at $t=0^\circ\text{C}$ if its density at the latter temperature is $1.632\ 55\ \text{g/cm}^3$. Neglect the compressibility of carbon tetrachloride within the indicated interval of pressures.

8. Find ΔG for the processes:



if $t_{\text{n.b.p.}}=80.1^\circ\text{C}$. Consider the benzene vapour to be an ideal gas.

What conclusion can be reached on the direction of the processes using the results obtained?

9. Find ΔG and ΔA for a process in which one mole of liquid benzene at $t=99.9^\circ\text{C}$ and $p=15$ atm is isothermally converted into saturated vapour; at this temperature the isothermal compressibility $\kappa=187\times 10^{-6}\ \text{atm}^{-1}$, the densities of the boiling liquid and the saturated vapour are respectively equal to 0.7927 and $0.0047\ \text{g/cm}^3$, and the temperature dependence of the vapour pressure is expressed by the equation

$$\log p\ (\text{mm Hg}) = -\frac{1686.77}{T} + 7.6546$$

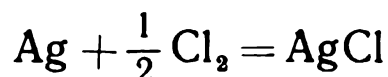
The density of liquid benzene at $t=99.9^\circ\text{C}$ extrapolated for $p=0$ is approximately equal to $0.9\ \text{g/cm}^3$.

10. The minimum work needed for the reversible isothermal separation of one mole of a binary ideal solution into the pure components (considering the vapour to be ideal gases and neglecting the volume of the liquid) is expressed by the equation

$$W_{\min} = RT [x_1 \ln x_1 + (1-x_1) \ln (1-x_1)]$$

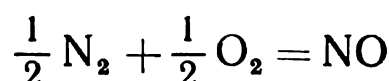
Find the work of separating an equimolar solution at 25°C .

11. The e.m.f. of a cell in which the reaction



proceeds is equal to $1.132\ \text{V}$ at 17°C . Find ΔG and ΔA . Neglect the volume of the silver and silver chloride. Consider the chlorine to be an ideal gas.

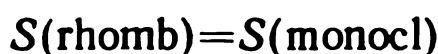
12. The entropies of nitrogen, oxygen and nitrogen oxide at $t=25^\circ\text{C}$ and $p=1$ atm are respectively 45.78 , 49.06 and $50.34\ \text{cal/mol}\cdot\text{K}$. Find ΔG at $t=200^\circ\text{C}$ and $p=1$ atm for the reaction



if at $p=1$ we have $\Delta G_{298}=20\ 660\ \text{cal/mol}$. Consider that the rate of change of ΔG with the temperature in the interval from 298 to $473\ \text{K}$ is constant.

13. At $t=25^\circ\text{C}$ the entropy of rhombic sulphur is 7.62, and that of monoclinic sulphur is 7.78 cal/g-atom \cdot K. The heats of combustion are respectively $-70\,940$ and $-71\,020$ cal/mol.

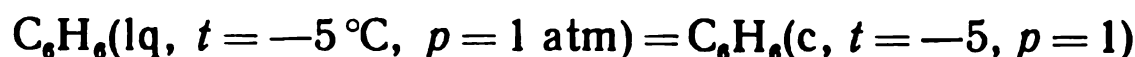
Find ΔG and ΔA for the process



Neglect in the first approximation the difference between the densities of rhombic and monoclinic sulphur.

What conclusion can be made from the result obtained?

14. Using the results obtained in solving Example 4, find the change in the enthalpy in the process



if $\Delta S = -8.48$ cal/mol \cdot K (see the solution of Example 13 in Sec. 3.1).

Compare the result of the calculations with the value found thermochemically (-2360 cal/mol, see the solution of the same example).

15. Calculate W , Q , ΔH , ΔU , ΔS , ΔA and ΔG for the isothermal compression of an ideal gas from $p_1=0.05$ to $p_2=0.1$ atm at $t=500^\circ\text{C}$.

16. Prove the truth of the following relationships:

$$U = G - T \left(\frac{\partial G}{\partial T} \right)_p - p \left(\frac{\partial G}{\partial p} \right)_T \quad (\text{a})$$

$$dG = V \left(\frac{\partial p}{\partial V} \right)_T dV + \left[V \left(\frac{\partial p}{\partial T} \right)_V - S \right] dT \quad (\text{b})$$

$$C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_V \quad (\text{c})$$

$$C_p - C_V = -T \frac{(\partial^2 A / \partial T \partial V)^2}{(\partial^2 A / \partial V^2)_T} \quad (\text{d})$$

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p \quad (\text{e})$$

$$\left(\frac{\partial U}{\partial V} \right)_S = \left(\frac{\partial A}{\partial V} \right)_T \quad (\text{f})$$

$$\left(\frac{\partial H}{\partial p} \right)_S = \left(\frac{\partial G}{\partial p} \right)_T \quad (\text{g})$$

$$\left(\frac{\partial A}{\partial T} \right)_V = \left(\frac{\partial G}{\partial T} \right)_p \quad (\text{h})$$

17. Show that for an ideal gas

$$\left(\frac{\partial G}{\partial T} \right)_V = -S + R$$

and

$$\left(\frac{\partial G}{\partial V} \right)_T = -p$$

Use the concept of the characteristic functions for the solution.

18. Show that H is a characteristic function at variable p and S .

* See Eq. (d) in the initial conditions of Problem 6, Sec. 3.1.

Chapter Four

REAL GASES

4.1. PRESSURE-VOLUME-TEMPERATURE-COMPOSITION RELATIONSHIPS

The relationship between p , V and T for a *gas* at moderate pressures can be found by the *van der Waals equation*

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (4.1)^*$$

and the *Berthelot equation*

$$pV = RT \left[1 + \frac{9pT_{cr}}{128T\rho_{cr}} \left(1 - 6 \frac{T_{cr}^2}{T^2} \right) \right] \quad (4.2)$$

at high pressures—by the *Beattie-Bridgeman equation*

$$pV^2 = RT \left[V + B_0 \left(1 - \frac{b}{V} \right) \right] \left(1 - \frac{c}{VT^3} \right) - A_0 \left(1 - \frac{a}{V} \right) \quad (4.3)$$

and at very high pressures—by the *Rosen equation*

$$pV = A + Bp + CT \quad (4.4)$$

The compressibility of a gas is calculated according to experimental data on the basis of the value of the compression factor

$$Z \equiv \frac{pV}{RT} \quad (4.5)$$

The relationship between p , V , T and the composition of *gas mixtures* is determined in several ways, for example:

(1) by combining the law of additivity of the partial pressures (*Dalton's law*)

$$p = \sum p_i \text{ or } p_i = x_i p \quad (4.6)$$

with an equation of state of a pure gas;

(2) by combining the law of additivity of the partial volumes (*Amagat's law*)

$$V = \sum V_i \text{ or } V_i = x_i V \quad (4.7)$$

with an equation of state of a pure gas;

* The values of the constants a and b needed for calculations are given in Appendix 7, and the values of p_{cr} and t_{cr} in Appendix 8.

(3) by combining the constants of an equation of state of a pure gas; for example, it is possible to use Eq. (4.3) in which

$$\begin{aligned} A_0 &= [\sum x_i V(\overline{A_0})_i]^2; & a &= \sum x_i a_i; \\ B_0 &= \sum x_i (B_0)_i; & b &= \sum x_i b_i \quad \text{and} \quad c = \sum x_i c_i \end{aligned} \quad (4.8)$$

(4) according to the compression factor of gas mixtures;

(5) according to the equations of state of gas mixtures, in particular by the *Bartlett equation*

$$p = p_1^\circ x_1 + p_2^\circ x_2 + \dots \quad (4.9)$$

(6) according to the *Krichevsky-Kazarnovsky equation*, which for binary mixtures acquires the following form:

$$p = p_1^\circ x_1 + p_2^\circ x_2 + ax_1 x_2 (p_1^\circ - p_2^\circ) \quad (4.10)$$

In Eqs. (4.9) and (4.10) the values of p , p_1° and p_2° are taken at the same molar volume (equal to the molar volume of the mixture).

For the calculation of the relationships p - V - T and p - V - T - x see also Sec. 6.1.

Examples

1. Using Eq. (4.1), find what volume one kilogram of methane should occupy for its pressure to be 400 atm at $t=0^\circ\text{C}$.

Compare the result of the solution with calculations according to the Mendeleev-Clapeyron equation and with the value $V=58.52\text{ cm}^3/\text{mol}$ found experimentally.

Solution. We perform the calculations by the method of trial and error. For orientation let us assume that

$$V = \frac{RT}{p} + a = \frac{82.06 \times 273.2}{400} + 42.78 = 56.05 + 42.78 = 98.83\text{ cm}^3/\text{mol}$$

hence

$$p = \frac{82.06 \times 273.2}{98.83 - 42.78} - \frac{2.264 \times 10^6}{98.83^2} = 168.2\text{ atm}$$

which is lower than the given pressure.

Assume that $V=60\text{ cm}^3/\text{mol}$; consequently,

$$p = \frac{82.06 \times 273.2}{60 - 42.78} - \frac{2.264 \times 10^6}{60^2} = 673\text{ atm}$$

which considerably exceeds the given pressure.

Assume that $V=70$; hence

$$p = \frac{82.06 \times 273.2}{70 - 42.78} - \frac{2.264 \times 10^6}{70^2} = 361.6\text{ atm}$$

which is lower than the given pressure.

Assume that $V=65$; hence

$$p = \frac{82.06 \times 273.2}{65 - 42.78} - \frac{2.264 \times 10^6}{65^2} = 473.1 \text{ atm}$$

By interpolation using a plot of V versus p (Fig. 7) we find $V \approx 67.9$, which differs from the experimental value by 16%. Such a considerable deviation is due to the fact that the pressure is very great.

The volume of one kilogram of methane (whose molecular weight is 16.04) is

$$\frac{67.9}{16.04} \times \frac{1000}{1000} = 4.23 \text{ dm}^3$$

Calculation by the Mendeleev-Clapeyron equation yields

$$V = \frac{82.06 \times 273.2}{400} = 56.05 \text{ cm}^3/\text{mol}$$

which differs from the experimental value by 4.2%.

Good agreement of the value calculated by the less accurate equation with the experimental one is explained by the fact that at pressures close to $p=400$ atm the isotherm $pV=f(p)$ (for $t=0^\circ\text{C}$) for methane passes near the horizontal line $pV=f(p)$ of an ideal gas.

2. Using the data on the compressibility of ethane at $t=204.4^\circ\text{C}$ given in Fig. 8, find the pressure in a reservoir with a volume of 0.5 m^3 if it contains 100 kg of ethane.

Solve the same problem graphically.

Solution. The molar volume, with the molecular weight of ethane equal to 30.07, is

$$V = \frac{0.5 \times 1000 \times 1000}{100 \times 1000} \times \frac{1000}{30.07} = 150.3$$

therefore in accordance with Eq. (4.5) we have

$$p = \frac{82.06 \times 477.6}{150.3} Z = 260.7 Z$$

We perform the calculations by the method of successive approximations. For orientation we assume that $Z=1$, whence $p=260.7$ atm. In Fig. 8 the value of $Z=0.888$ corresponds to this pressure, which differs from the assumed value.

We assume $Z=0.86$; consequently $p=224.2$ atm. From Fig. 8 we have $Z=0.858$.

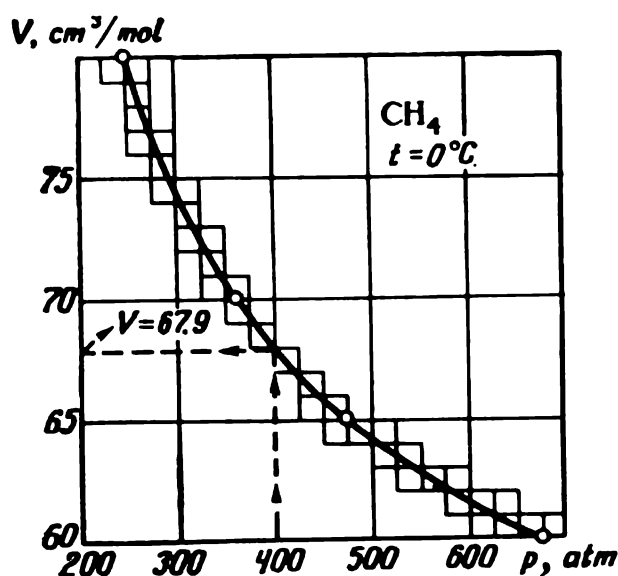


Fig. 7

We finally assume that $p=224$ atm.

Graphical solution: we rewrite the found equation relating p and Z in the form

$$Z=0.003\ 84p$$

Straight line AB (Fig. 8) corresponds to this equation; it intersects the isotherm $Z=f(p)$ at the point where $Z=0.858$ and $p=224$ (point O).

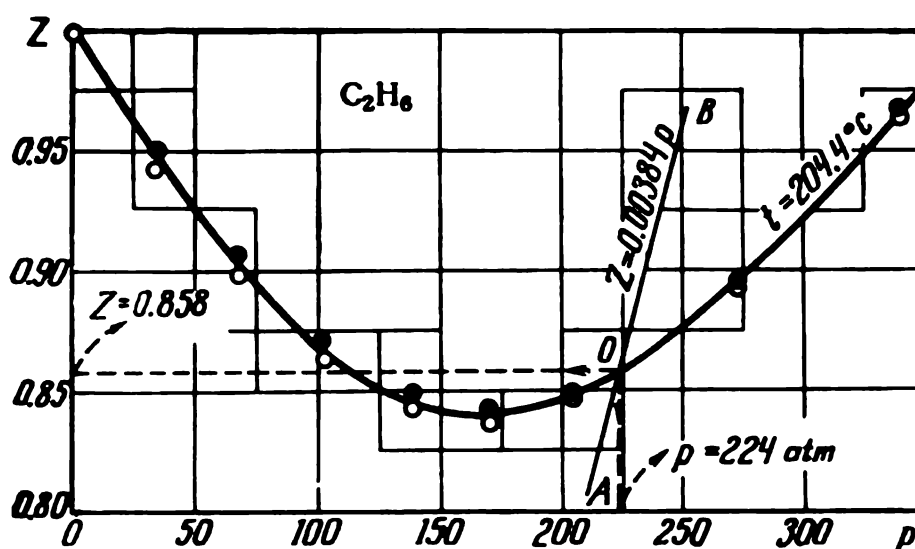


Fig. 8

3. Find the temperature in a reservoir having a capacity of 20 dm^3 and containing 5 kilograms of propane at a pressure of 100 atm on the basis of the data given below.

$t, ^\circ\text{C}$	100	107.8	125	150	200	253.2	297.3	336.2
$Z_{p=100}$	0.3563	0.3696	0.3913	0.4726	0.6642	0.7932	0.8603	0.8962

Solution. In accordance with Eq. (4.5) we have

$$T = \frac{pV}{ZR} = \frac{100 \times \frac{20}{5 \times 1000} \times 44.09}{Z \times 0.08206} = \frac{215}{Z} \quad \text{or} \quad Z = \frac{215}{T}$$

Now we plot a chart of Z versus t according to the data given in the initial conditions (Fig. 9, curve KL). We plot the curve corresponding to the equation found (curve AB) on it. The intersection of these two curves gives the sought result, namely, $t=157^\circ\text{C}$.

If in these conditions the propane had the properties of an ideal gas ($Z=1$), then the temperature would equal 215 K (-58°C).

4. What pressure should a mixture containing nitrogen and hydrogen in the proportion of 1 : 3 be compressed to for V to equal $54.6\text{ cm}^3/\text{mol}$ at $t=0^\circ\text{C}$?

Perform the calculations according to the equation found by the simultaneous solution of Eqs. (4.1) and (4.7).

Compare the result of the calculations with the experimentally found value of $p=600$ atm.
Solution. Since

$$V = x_1V_1^\circ + x_2V_2^\circ$$

where V_1° and V_2° are the molar volumes of the pure components at a

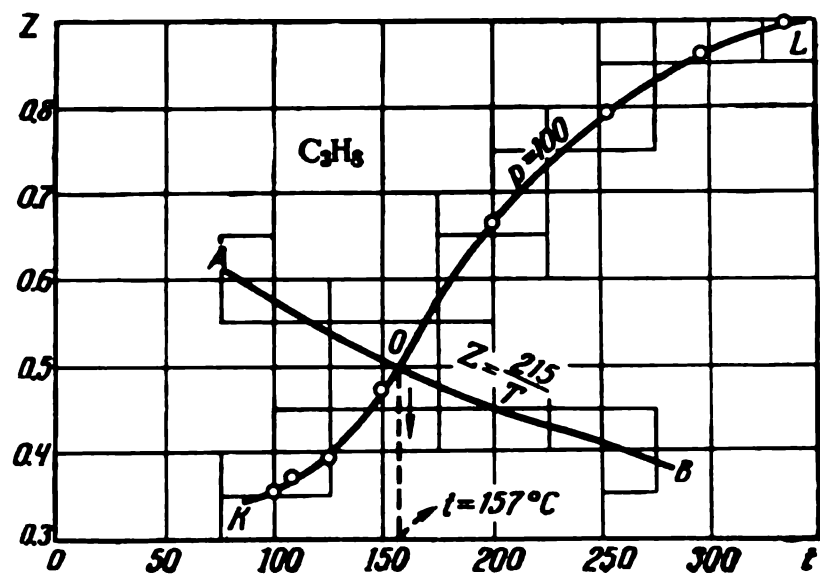


Fig. 9

pressure equal to that of the mixture, then

$$54.6 = 0.25V_{N_2}^\circ + 0.75V_{H_2}^\circ,$$

$$V_{H_2}^\circ = 72.8 - 0.333V_{N_2}^\circ,$$

The calculations consist in finding such values of $V_{N_2}^\circ$ and $V_{H_2}^\circ$, whose introduction into Eq. (4.1) would give $p_{N_2}^\circ = p_{H_2}^\circ$; we perform it by trial and error (see Table 8).

Table 8

Assumed value of	Values obtained		
$V_{N_2}^\circ$	$V_{H_2}^\circ$	$p_{N_2}^\circ$	$p_{H_2}^\circ$
55	54.48	921.4	721.6
60	52.82	673.2	767.2
57	53.82	803.5	739.0
58.5	53.32	732.6	752.8

Next we plot $p_{N_2}^\circ$ against $p_{H_2}^\circ$ (Fig. 10) and find the point at which $p_{H_2}^\circ = p_{N_2}^\circ = 749$ atm, which differs from the experimentally found value by 24.8%.

Such a considerable deviation is first of all due to the inaccuracy of Eq. (4.1) at very high pressures.

5. The pressure dependence of the molar volumes of methane and hydrogen at 0°C is shown by the following data:

p , atm	80	120	160	200	250	300	400	500	600
$V_{CH_4}^\circ$, cm ³ /mol	229.0	141.2	103.4	85.31	73.31	66.44	58.52	54.05	51.09
$V_{H_2}^\circ$, cm ³ /mol						90.17	71.70	60.52	53.13

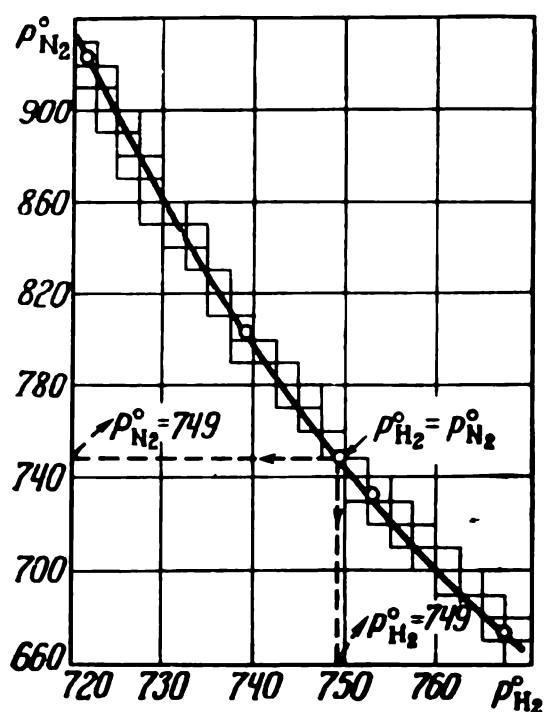


Fig. 10

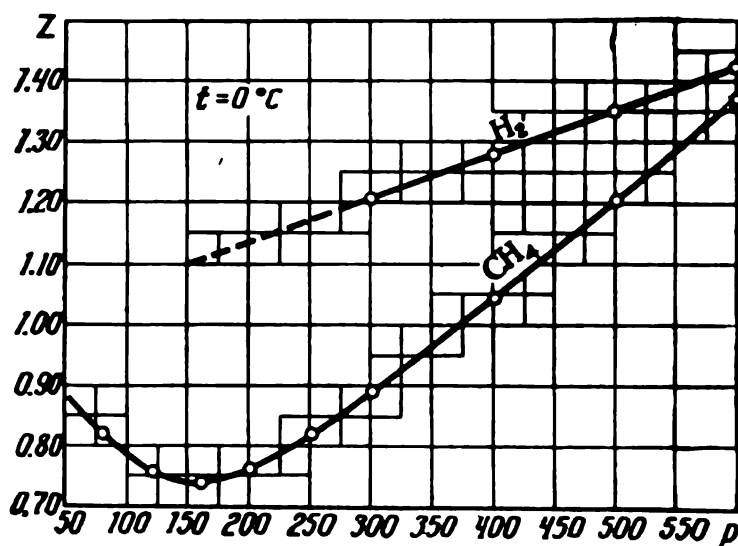


Fig. 11

What should the pressure of a mixture consisting of 33.1% methane and 66.9% hydrogen be for one mole of it to occupy a volume of 58.72 cm³ at 0°C ? Perform the calculations according to the compression factor, using Eq. (4.7).

Compare the result of the calculations with the experimentally found value (500 atm).

Solution. Using the values of the volumes given in the initial conditions of the example and Eq. (4.5), we calculate the values of Z_{CH_4} and Z_{H_2} and get the following results:

p , atm	80	120	160	200	250	300	400	500	600
Z_{CH_4}	0.817	0.756	0.738	0.761	0.817	0.889	1.041	1.205	1.367
Z_{H_2}						1.207	1.279	1.350	1.422

Next we plot the isotherms $Z=f(p)$ (Fig. 11) and using the method of successive approximations find with the aid of the drawing the pressure of the gas mixture.

Assume that $p=500$ atm. Hence $Z_{\text{CH}_4}=1.2055$ and $Z_{\text{H}_2}=1.350$. Therefore

$$Z = x_{\text{CH}_4}Z_{\text{CH}_4} + x_{\text{H}_2}Z_{\text{H}_2} = 0.331 \times 1.2055 + 0.669 \times 1.350 = 1.301$$

and

$$p = \frac{ZRT}{V} = \frac{1.301 \times 82.06 \times 273.2}{58.72} = 496.7 \text{ atm}$$

which differs from the assumed value.

If we assume that $p=490$ atm, then

$$Z = 0.331 \times 1.188 + 0.669 \times 1.343 = 1.292$$

and

$$p = \frac{1.292 \times 82.06 \times 273.2}{58.72} = 493.3 \text{ atm}$$

which also does not coincide with the assumed value of p .

Assume that $p=480$ atm. Hence

$$Z = 0.331 \times 1.173 + 0.669 \times 1.336 = 1.282$$

and $p=489.5$ atm.

Interpolation gives us the final value of $p \approx 495.3$ atm, which differs from the experimentally found value by 0.94%.

6. Solve Example 5 using the compression factor of the mixture and Eq. (4.6). Take the compression factors of methane and hydrogen given in Fig. 11 for the calculations.

Solution.

$$V_{\text{CH}_4}^\circ = \frac{58.72}{0.331} = 177.4 \text{ and } V_{\text{H}_2}^\circ = \frac{58.72}{0.669} = 87.77 \text{ cm}^3/\text{mol}$$

In accordance with Eq. (4.5)

$$Z_{\text{CH}_4} = \frac{p_{\text{CH}_4} \times 177.4}{82.06 \times 273.2} = 0.007913 p_{\text{CH}_4}$$

and

$$Z_{\text{H}_2} = \frac{p_{\text{H}_2} \times 87.77}{82.06 \times 273.2} = 0.003915 p_{\text{H}_2}$$

Assume that $p_{\text{CH}_4}=80$ atm. Hence

$$\text{from Fig. 11 } Z_{\text{CH}_4} = 0.817$$

$$\text{by Eq. (4.5) } Z_{\text{CH}_4} = 0.633$$

Assume that $p_{\text{CH}_4}=120$ atm. Hence

$$\text{from Fig. 11 } Z_{\text{CH}_4} = 0.756$$

$$\text{by Eq. (4.5) } Z_{\text{CH}_4} = 0.9496$$

Assume that $p_{\text{CH}_4}=100$ atm. Hence

$$\begin{aligned} &\text{from Fig. 11} \quad Z_{\text{CH}_4}=0.782 \\ &\text{by Eq. (4.5)} \quad Z_{\text{CH}_4}=0.7913 \end{aligned}$$

We use the values of p and Z_{CH_4} obtained to plot curves of the pressure dependence of Z_{CH_4} found from Fig. 11 and by Eq. (4.5). The intersection of these curves corresponds to the sought values $Z_{\text{CH}_4}=0.786$ and $p_{\text{CH}_4}=99.3$ atm.

Assume that $p_{\text{H}_2}=400$ atm. Hence

$$\begin{aligned} &\text{from Fig. 11} \quad Z_{\text{H}_2}=1.279 \\ &\text{by Eq. (4.5)} \quad Z_{\text{H}_2}=1.566 \end{aligned}$$

Assume that $p_{\text{H}_2}=300$ atm. Hence

$$\begin{aligned} &\text{from Fig. 11} \quad Z_{\text{H}_2}=1.207 \\ &\text{by Eq. (4.5)} \quad Z_{\text{H}_2}=1.174 \end{aligned}$$

Assume that $p_{\text{H}_2}=350$ atm. Hence

$$\begin{aligned} &\text{from Fig. 11} \quad Z_{\text{H}_2}=1.242 \\ &\text{by Eq. (4.5)} \quad Z_{\text{H}_2}=1.370 \end{aligned}$$

By graphical interpolation (see above) we get $Z_{\text{H}_2}=1.215$ and $p_{\text{H}_2}=310.3$ atm. Consequently

$$p=99.3+310.3=409.6 \text{ atm}$$

which differs from the experimental value by 18.1%.

A comparison of the results obtained in solving Examples 5 and 6 shows that for the mixture being considered in the given conditions Eq. (4.7) holds and that the accuracy of Eq. (4.6) is not sufficient.

7. Use Eq. (4.9) to calculate the pressure at which a mixture consisting of 33.1% methane and 66.9% hydrogen should be at 0°C for the volume to be $58.72 \text{ cm}^3/\text{mol}$.

Use the following data on the compressibility of methane and hydrogen at 0°C for the calculations:

p , atm	250	300	400	500	600	700
$V_{\text{CH}_4}^\circ$, cm^3/mol . . .	73.31	66.44	58.52	54.05	51.09	
$V_{\text{H}_2}^\circ$, cm^3/mol			71.70	60.52	53.13	47.91

Compare the result obtained in the solution with the experimental value of $p=500$ atm and with the results of solving Examples 5 and 6.

Solution. We plot the values of $V_{\text{CH}_4}^\circ$ and $V_{\text{H}_2}^\circ$ (Fig. 12) and find by interpolation that at $V=58.72 \text{ cm}^3/\text{mol}$ we have $p_{\text{H}_2}^\circ=519$ and $p_{\text{CH}_4}=396$ atm.

For this reason in accordance with Eq. (4.9)

$$p=519\times0.669+396\times0.331=478.3\text{ atm}$$

which differs from the experimental value by 4.3%.

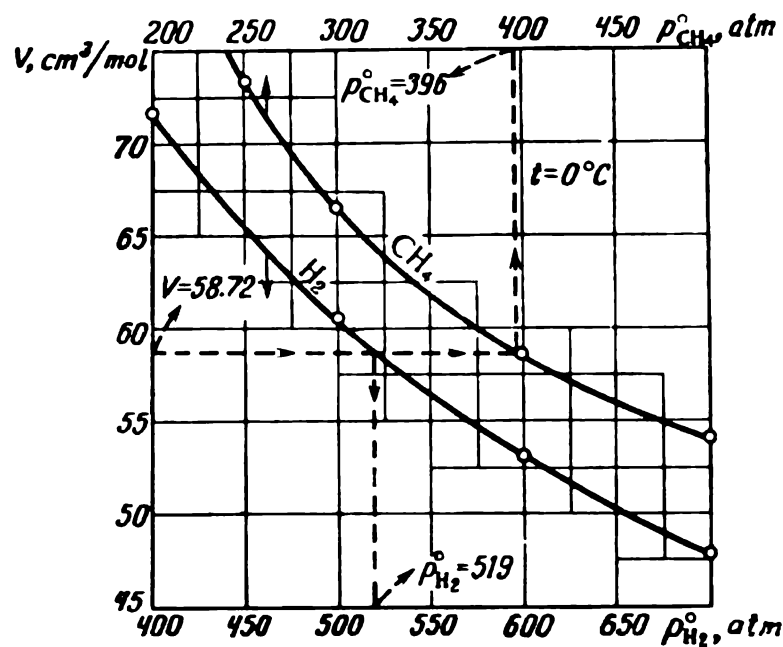


Fig. 12

8. The pressures of nitrogen, hydrogen and a nitrogen-hydrogen mixture (1 : 3) calculated at the same densities according to the corresponding pressure coefficients are

ρ , g/cm ³	0.0010	0.0010	0.0018	0.0018
t , °C	−100	−50	0	100
$\rho_{N_2}^\circ$, atm	377	170	631	1013
$\rho_{H_2}^\circ$, atm	367	214	567	782
p , atm	369	207	578	818

Find: (1) equation (4.10) for the nitrogen-hydrogen mixture; (2) the pressure of the mixture corresponding at $t=0^\circ\text{C}$ to its molar volumes of 57.82, 54.60, 49.54 and 45.75 cm³.

Use the following experimental data on the compressibility of nitrogen and hydrogen at $t=0^\circ\text{C}$ for the calculations:

p , atm	500	600	800	1000
Z_{N_2}	1.3885	1.5214	1.7959	2.0641
Z_{H_2}	1.3500	1.4226	1.5665	1.7101

Compare the results of the calculations with the experimental data respectively equal to 550, 600, 700 and 800 atm.

Solution. (1) Using the data given above, we calculate

$$\Delta = \frac{p - (0.25\rho_{N_2}^\circ + 0.75\rho_{H_2}^\circ)}{0.25 \times 0.75}$$

depending on $p_{H_2}^\circ - p_{N_2}^\circ$. We get the following values:

$p_{H_2}^\circ - p_{N_2}^\circ$	44	-10	-64	-231
Δ	21.3	-2.7	-26.7	-116.0

Next we plot a chart in the coordinates Δ versus $p_{H_2}^\circ - p_{N_2}^\circ$ (Fig. 13). Through the points obtained (and through the origin of coordinates) we draw a straight line. Its slope is $a \approx 0.5$. Consequently, Eq. (4.10) acquires the form

$$p = 0.25p_{H_2}^\circ + 0.75p_{N_2}^\circ + 0.5x_{H_2}x_{N_2}(p_{H_2}^\circ - p_{N_2}^\circ)$$

(2) After calculating the molar volumes of nitrogen and hydrogen according to the compression factors given in the initial conditions at the indicated pressures, we plot a chart (Fig. 14). Next drawing isochores corresponding to the molar volumes of the mixture indicated in

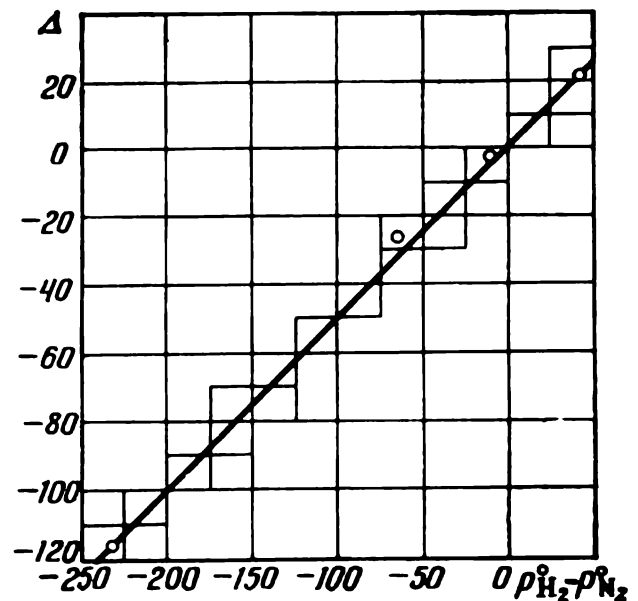


Fig. 13

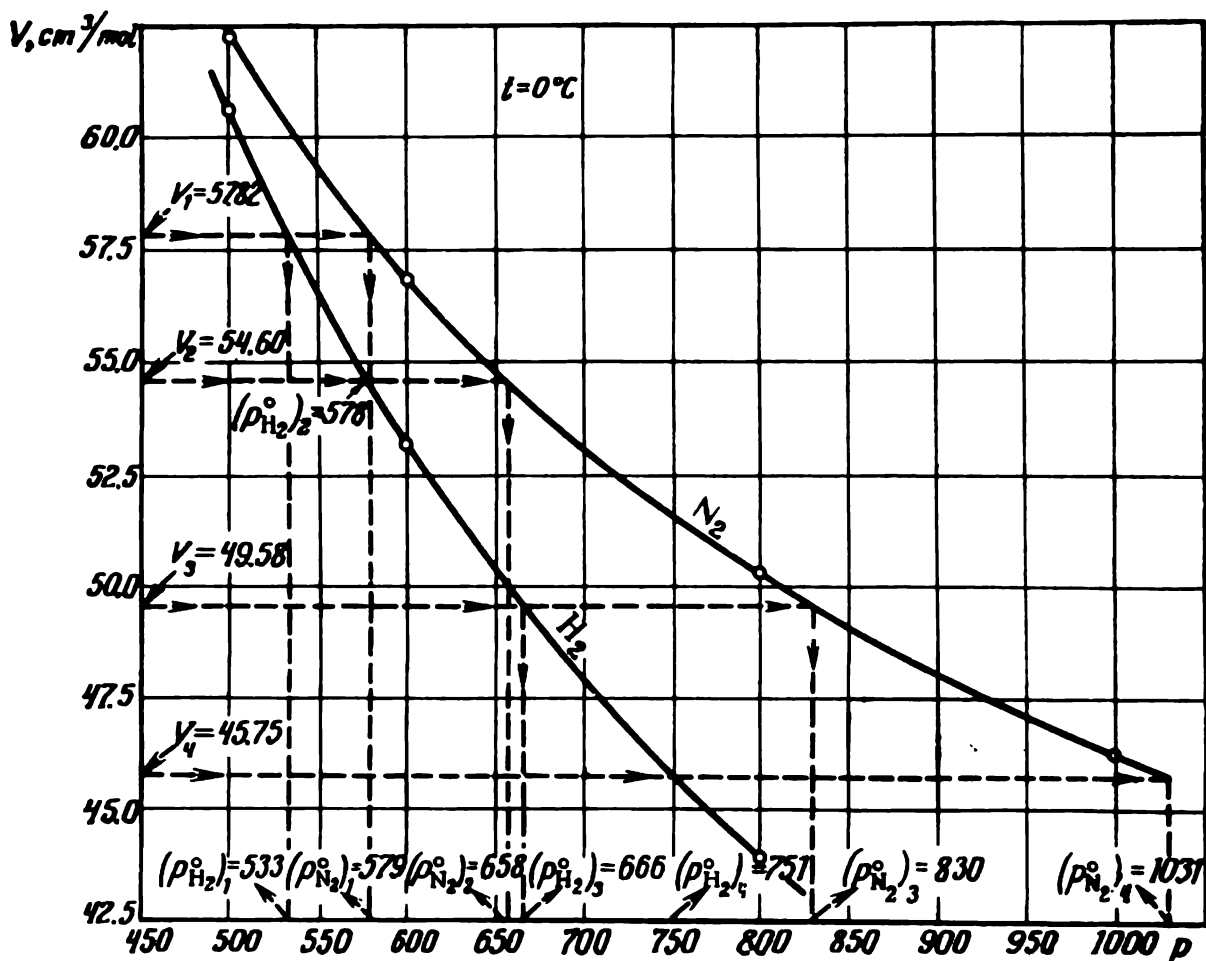


Fig. 14

the initial conditions of the example, we get:

V_0 , cm ³ /mol	57.82	54.60	49.54	45.75
p_{N_2} , atm	579	658	830	1031
p_{H_2} , atm	533	578	666	751

Now we use the found equation to calculate the pressure of the mixture:

$$p_{V=57.82} = 0.25 \times 579 + 0.75 \times 533 + 0.5 \times 0.188 (-46) = 540.2 \text{ atm}$$

$$p_{V=54.60} = 0.25 \times 658 + 0.75 \times 578 + 0.5 \times 0.188 (-80) = 590.5 \text{ atm}$$

$$p_{V=49.54} = 0.25 \times 830 + 0.75 \times 666 + 0.5 \times 0.188 (-164) = 691.6 \text{ atm}$$

$$p_{V=45.75} = 0.25 \times 1031 + 0.75 \times 751 + 0.5 \times 0.188 (-280) = 794.7 \text{ atm}$$

The mean error of the calculations is 1.31%.

Problems

1. Use Eqs. (4.1) and (4.2) to find the pressure at which methane is at $t=25^\circ\text{C}$ if $V=267 \text{ cm}^3$.

Compare the result with the value calculated by the Mendeleev-Clapeyron equation and with the experimentally found value $p=80 \text{ atm}$.

2. What will the form of the line obtained be if we plot isochores for a gas following Eq. (4.1) in the coordinates p - T ?

3. One of the limiting conditions which any equation of state of a real gas must satisfy is the one that

$$\lim_{1/T \rightarrow 0} \frac{V}{T} = \frac{R}{p}$$

Show that Eq. (4.1) meets this condition.

4. Show that at low pressures Eq. (4.1) can be used in the form

$$pV = RT(1 - Bp), \text{ where } B = \frac{1}{RT} \left(\frac{a}{RT} - b \right)$$

Perform the calculations proposed in Example 1 with the aid of this equation. Compare the results of the calculation with those obtained in solving the cited example.

5. The critical point is the point of inflection on the isotherm p - V .

1. Find the values of the critical parameters if Eq. (4.1) holds for a substance.

2. Show that the constants of this equation of state are

$$a = \frac{27R^2T_{cr}^2}{64p_{cr}} \text{ and } b = \frac{RT_{cr}}{8p_{cr}}$$

6. Equation (4.2) in its original form was as follows:

$$\left(p + \frac{a}{TV^2}\right)(V-b) = RT$$

where

$$a = \frac{16}{3} p_{\text{cr}} V_{\text{cr}}^2 T_{\text{cr}}; \quad b = \frac{1}{4} V_{\text{cr}} \quad \text{and} \quad R = \frac{32}{9} \frac{p_{\text{cr}} V_{\text{cr}}}{T_{\text{cr}}}$$

As a result of what assumptions will Eq. (4.2) be obtained from the equation given in the initial conditions of the present problem?

7. Under what pressure is methanol if its density at 270°C is 0.09 g/cm³?

Use Eq. (4.3) for the calculations. The following constants of Eq. (4.3) have been obtained for methanol: $A_0=33.309$, $a=0.092463$, $B_0=0.60362$, $b=0.099268$ and $c=320310$ ($R=0.08206$).

Compare the result with the experimental value of $p=81.90$ atm.

8. In addition to the compression factor determined by Eq. (4.5), a compression factor is also used that is determined by the formula

$$Z' = \frac{pV}{p_0V_0}$$

where p_0V_0 is the product pV at $t=0^\circ\text{C}$ and $p=1$ atm.

Find the equation relating Z and Z' .

9. For hydrogen Eq. (4.4) can be written as follows (see Problem 8):

$$Z' = 0.990 + 0.721 \times 10^{-3}p + 0.376 \times 10^{-2}t$$

Find V_{H_2} at $p=1000$ atm and $t=25^\circ\text{C}$.

Compare the result of the calculations with the experimental value of $V=48.82$ cm³.

10. With the aid of the data obtained in solving Problem 5, determine what the compression factor Z should be at the critical point if Eq. (4.1) holds for a gas.

Compare the result of the solution with the calculations by Eq. (4.5) on the basis of the data given below (for the values of p_{cr} and t_{cr} see Appendix 8).

Substance . . .	CH ₄	C ₂ H ₆	C ₂ H ₄	CO	CO ₂	Cl ₂	Ne	O ₂	SO ₂
V_{cr}	99.2	137	134	89.9	96.1	124	41	74.3	126

11. Show that if Eqs. (4.1) and (4.6) hold for a gas mixture, then

$$p = RT \sum \frac{x_i}{V - x_i b_i} - \frac{1}{V^2} \sum a_i x_i^2$$

12. What pressure should one mole of a nitrogen-hydrogen mixture (1 : 3) be compressed to for its volume at 0°C to be 54.6 cm³?

Use the equation found in solving the previous problem for the calculations.

Compare the result of the calculations with the value obtained on the assumption that the mixture is an ideal one and with the result of solving Example 4. The experimentally found value is 600 atm.

13. Find the pressure at which one mole of a mixture consisting of 53% methane and 47% nitrogen should be for its volume to equal 159 cm³ at $t=100^{\circ}\text{C}$. Use Eq. (4.8) for the calculations with $(A_0)_{\text{CH}_4}=2.2769$, $a_{\text{CH}_4}=18.55\times 10^{-3}$, $(B_0)_{\text{CH}_4}=55.87\times 10^{-3}$, $b_{\text{CH}_4}=-15.87\times 10^{-3}$, $c_{\text{CH}_4}=128\,300$, and $(A_0)_{\text{N}_2}=1.3445$, $a_{\text{N}_2}=26.17\times 10^{-3}$, $(B_0)_{\text{N}_2}=50.46\times 10^{-3}$, $b_{\text{N}_2}=-6.91\times 10^{-3}$, $c_{\text{N}_2}=42\,000$ ($R=0.082\,06$).

Compare the result of the calculations with the experimentally found value of $p=200$ atm.

14. Find the pressure at which a mixture consisting of 64.4% hydrogen, 25.0% nitrogen and 10.6% methane is if at $t=0^{\circ}\text{C}$ its volume corresponds to the value of $Z'=1.3653$ (see Problem 8).

For a triple mixture Eq. (4.10) becomes

$$p = p_1^{\circ}x_1 + p_2^{\circ}x_2 + p_3^{\circ}x_3 + a_{1,2}x_1x_2(p_1^{\circ} - p_2^{\circ}) + a_{2,3}x_2x_3(p_2^{\circ} - p_3^{\circ}) + a_{1,3}x_1x_3(p_1^{\circ} - p_3^{\circ})$$

The coefficients of Eq. (4.10) for binary mixtures are $a_{\text{N}_2,\text{H}_2}=0.468$, $a_{\text{N}_2,\text{CH}_4}=0.464$ and $a_{\text{H}_2,\text{CH}_4}=0.560$.

The compressibility of pure hydrogen, nitrogen and methane is expressed by the following data:

p , atm	100	200	300	400
Z'_{H_2}	1.0639	1.1336	1.2045	1.2775
Z'_{N_2}	0.9848	1.0355	1.1335	1.2557
Z'_{CH_4}	0.7845	0.7631	0.8886	1.0468
p , atm	500	600	800	1000
Z'_{H_2}	1.3500	1.4226	1.5665	1.7101
Z'_{N_2}	1.3885	1.5214	1.7959	2.0641
Z'_{CH_4}	1.2086	1.3709	1.6894	2.0000

Compare the results of the calculations with that computed by Eq. (4.9) and with the experimentally found value of $p=500$ atm.

4.2. FUGACITY

The methods of calculating the fugacity are based on integration of the equations

$$\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{V}{RT} \tag{4.11}$$

and

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{H^{\circ} - H}{RT^2} \tag{4.12}$$

expressing the dependence of the fugacity on the pressure and the tem-

perature. In Eq. (4.12) the quantity $H^* - H$ is equal to the change in the molar enthalpy when a gas expands from the given to an infinitely small pressure.

Graphical calculations can be performed with the aid of the equation

$$RT \ln f = RT \ln p - \int_0^p \alpha dp \quad (4.13)$$

where

$$\alpha = \frac{RT}{p} - V \quad (4.14)$$

The quantity $\int_0^p \alpha dp$ is determined either as the area confined by the isobar p and isotherms of the ideal and real gases (up to their intersection), or, which is more convenient, as the area under the isotherm $\alpha = f(p)$ confined by the axis of ordinates and the isobar p .

The analytical method of calculating the fugacity is based on calculating $\int_1^2 V dp$ in Eq. (4.11) with the aid of an equation of state.

When it is more convenient to use the dependence of p on V instead of that of V on p , the following relationship can be used:

$$\ln f = \ln p^* + \frac{1}{RT} \left(pV - RT - \int_{V_\infty}^V p dV \right) \quad (4.15)$$

where V_∞ is the molar volume at an infinitely small pressure p^* .

At comparatively low pressures, an approximate equation is used for calculating the fugacity, namely,

$$f = \frac{p^2}{p_{id}} = pZ \quad (4.16)$$

where Z is the compression factor.

The fugacity of liquids and solids in equilibrium with their vapour is equal to the fugacity of the vapour. The calculation for another pressure is accomplished by integrating Eq. (4.11) within the limits from $p_{\text{sat. vap.}}$ to the given pressure p .

The temperature dependence of the fugacity is expressed by Eq. (4.12), which may be represented as follows

$$\left(\frac{\partial \ln f}{\partial T} \right)_p = \frac{1}{RT^2} \int_0^p (\mu C_p) dp \quad (4.17)$$

where μ is the Joule-Thomson coefficient.

The fugacity of a component of a gas mixture is calculated by the equation

$$RT \ln f_i = RT \ln p + RT \ln x_i - \int_0^p (V_{id} - \bar{V}_i) dp \quad (4.18)$$

where \bar{V}_i is the partial molar volume.

Approximate estimation is performed using the *fugacity rule*:

$$f_i = f_i^\circ x_i \quad (4.19)$$

where f_i° = fugacity of a pure component under the pressure of the mixture

x_i = mole fraction of the component.

The pressure dependence of the fugacity of a mixture component at $T, x=\text{const}$ is determined by Eq. (4.11) in which the molar volume V is replaced by the partial molar volume \bar{V}_i . The temperature dependence of the fugacity at $p, x=\text{const}$ is determined by Eq. (4.12), the numerator of whose right-hand part contains the difference between the enthalpy of a component of the mixture at an infinitely low pressure and its enthalpy at the given pressure. See also the calculations in Sec. 6.1.

Examples

1. Calculate the fugacity of ammonia at $t=200^\circ\text{C}$ and $p=100$ and 400 atm if we have

$p, \text{ atm}$. . .	20	60	100	150	200	250	300	400
$V, \text{ cm}^3$. . .	1866	570.8	310.9	176.7	107.4	74.18	59.60	47.68

Solution. On the basis of the data given in the initial conditions, we calculate the values of α by Eq. (4.14) and get the following results:

$p, \text{ atm}$	20	60	100	150	200	250	300	400
α	75.0	76.2	77.4	82.1	86.7	81.12	69.82	49.38

Next we plot the isotherm of α versus p (Fig. 15).

By graphical integration we find that

$$\int_0^{100} \alpha dp \approx 7590$$

Consequently, by Eq. (4.13) we have

$$\log f = \log 100 - \frac{1}{2.303 \times 82.06 \times 473.2} \times 7590 = 1.9151$$

whence $f=82.2$ atm.

In the same way we find that $f=187$ atm at $p=400$ atm.

2. Prove with the aid of Eq. (4.15) that the fugacity of a gas for which the equation of state (4.1) holds may be calculated by the formula

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV}$$

Solution. Since

$$p dV = \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV$$

then

$$\begin{aligned} \int_{V_{\infty}}^V p dV &= \int_{V_{\infty}}^V \frac{RT}{V-b} dV - \int_{V_{\infty}}^V \frac{a}{V^2} dV = RT \ln \frac{V-b}{V_{\infty}-b} + \\ &+ \frac{a}{V} - \frac{a}{V_{\infty}} \approx RT \ln \frac{V-b}{V_{\infty}} + \frac{a}{V} = RT \ln \frac{V-b}{RT} + RT \ln p^* + \frac{a}{V} \end{aligned}$$

From Eq. (4.1)

$$pV - RT = \frac{RTb}{V-b} - \frac{a}{V}$$

Therefore in accordance with Eq. (4.15) we have

$$\begin{aligned} \ln f &= \ln p^* + \frac{1}{RT} \left(\frac{RTb}{V-b} - \frac{a}{V} - \right. \\ &\left. - RT \ln \frac{V-b}{RT} - RT \ln p^* - \frac{a}{V} \right) \end{aligned}$$

or

$$\ln f = \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV}$$

3. The pressure of saturated steam at 155 °C is 5.54 kgf/cm² and the volume of the steam is 0.3464 m³/kg. Calculate the fugacity of boiling water at 155 °C.

Solution. Since the fugacity of a boiling liquid equals that of its saturated vapour, and since the pressure is not great, the calculation is performed by Eq. (4.16):

$$f = \frac{p^2}{p_{id}} = p^2 \frac{V}{RT} = \left(\frac{5.54}{1.033} \right)^2 \times \frac{0.3464 \times 18.02}{0.08206 \times 428.2} = 5.11 \text{ atm}$$

Consequently, in the given case the fugacity of water differs from the pressure of saturated steam by about 5%.

4. The fugacity of ammonia at 200 °C and $p=100$ atm is 82.2 atm (see the solution of Example 1).

Find f for ammonia at 225 °C and $p=100$ atm and compare the result with the exact value equal to 85.25 atm. Perform the calculations

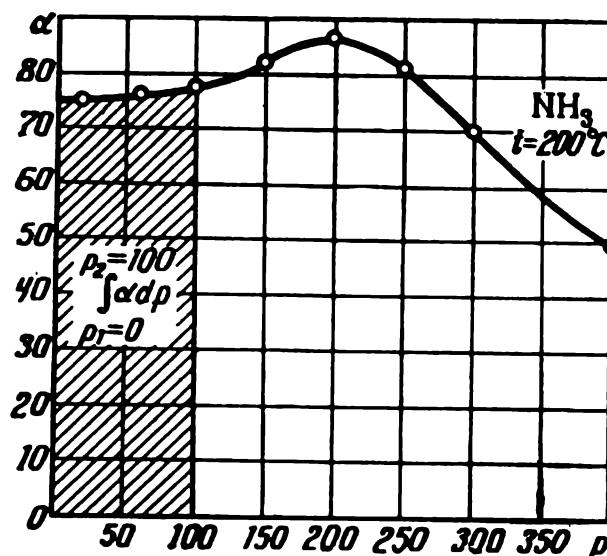


Fig. 15

with the aid of Eq. (4.12) and the equation

$$H_2 - H_1 = \frac{9}{128} \frac{RT_{cr}}{p_{cr}} \left(1 - 18 \frac{T_{cr}^2}{T^2} \right) (p_2 - p_1)$$

(see Example 2 in Sec. 4.4).

Solution. Integration of Eq. (4.12) yields

$$\ln \frac{f_{T_2}}{f_{T_1}} = \frac{H^* - H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

In the given case in accordance with the equation indicated above

$$H^* - H = \frac{9 \times 1.987 \times 405.6}{128 \times 111.5} \left(1 - \frac{18 \times 405.6^2}{473.2^2} \right) \times (0 - 100) = 621$$

Considering in the first approximation that this quantity is constant within the interval from 200 to 225 °C, we find

$$\log \frac{f_{498}}{82.2} = \frac{621}{4.576} \left(\frac{1}{473.2} - \frac{1}{498.2} \right) = \frac{621 \times 25}{4.576 \times 498.2 \times 473.2}$$

or

$$\log f_{498} = 1.9149 + 0.0144 = 1.9293 \quad \text{and} \quad f_{498} = 85.0 \text{ atm}$$

which differs from the exact value by 0.3%.

5. The compressibility of liquid ethyl ether at 0 °C within the pressure range from 1 to 1400 atm can be calculated by the equation

$$\frac{V}{M} = 0.7598 + \frac{425.89}{1779.3 + p}$$

Calculate the fugacity of the liquid ether at 0 °C and $p = 1000$ atm if at this temperature the pressure of its saturated vapour equals 185.3 mm Hg.

Solution. Integrating Eq. (4.11) within the limits from $p_{\text{sat. vap.}}$ to p , we get

$$RT \ln \frac{f}{f_{\text{sat. vap.}}} = \int_{p_{\text{sat. vap.}}}^p V dp$$

Assume that at $p = 185.3$ mm Hg (0.244 atm) the fugacity of the vapour is equal to its pressure. Hence

$$\log \frac{f}{0.244} = \frac{1}{2.303 \times 82.06 \times 273.2} \int_{0.244}^{1000} V dp$$

We determine the integral graphically. For this purpose we use the equation given in the initial conditions to calculate the specific volumes at pressures of 1, 200, 400, 600, 800 and 1000 atm and plot V

versus p . We get

$$\log f = \log 0.244 + \frac{74.12}{2.303 \times 82.06 \times 273.2 \times 950} = 0.7512$$

whence $f=5.62$ atm.

Problems

1. Use the results of solving Example 1 to find the change in the Gibbs energy in the isothermal expansion of one mole of ammonia from $p_1=400$ to $p_2=100$ atm if $t=200^\circ\text{C}$.

What would the change in the Gibbs energy be if in the indicated conditions ammonia could be considered as an ideal gas?

2. Calculate the fugacity of ammonia at 200°C and 100 atm with the aid of the equation derived in solving Example 2 and compare it with the value found in solving Example 1 if $V=310.9$ cm³.

Compare the result with the exact value of $f=82.2$ atm (see the solution of Example 1).

3. The values of α for methane at 0°C are $\alpha_{p=80}=51.20$ and $\alpha_{p=120}=45.60$. Find the constants of Eq. (4.1) for methane and calculate the fugacity at $p=40, 80, 120, 160$ and 200 atm.

Compare the results with the exact values respectively equal to 36.28, 65.94, 90.72, 112.3 and 132.6 atm.

4. Prove with the aid of Eq. (4.11) that when Eq. (4.2) holds, the fugacity of a gas may be calculated by the equation

$$\ln f = \ln p + \frac{9T_{cr}}{128p_{cr}T} \left(1 - 6 \frac{T_{cr}^2}{T^2} \right) p$$

Calculate the fugacity of ammonia at 200°C and 100 atm with the aid of this equation. For the values of t_{cr} and p_{cr} see Appendix 8. Compare the result of the solution with the exact value of $f=82.2$ atm (see the solution of Example 1) and with the result obtained in solving Problem 2.

5. Show using Eq. (4.11) that the fugacity of a gas for which Eq. (4.3) holds written in the form

$$p = \frac{RT}{V} + \frac{\beta}{V^2} + \frac{\gamma}{V^3} + \frac{\delta}{V^4}$$

can be calculated by the equation

$$\ln f = \ln RT - \ln V + \frac{1}{RTV} \left(2\beta + \frac{3\gamma}{2V} + \frac{4\delta}{3V^2} \right)$$

where

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}, \quad \gamma = -RTB_0b + A_0a - \frac{RB_0c}{T^2}, \quad \delta = \frac{RB_0bc}{T^2}$$

Use the equation found to calculate the fugacity of methanol at $t=300^\circ\text{C}$ and $p=200$ atm if $V=114$ cm³.

Take the constants of Eq. (4.3) needed for the calculations from the initial conditions of Problem 7 of Sec. 4.1. Express the volume in dm³.

6. Find the fugacity of ammonia at $t=200^\circ\text{C}$ and $p=100$ atm with the aid of Eq. (4.16) if $V=310.9$ cm³.

Compare the result of the calculations with the exact value of $f=82.2$ atm and with the results of the solution of Problems 2 and 4.

7. Use Eq. (4.13) to show that

$$\ln f = \ln p - \int_0^p (1-Z) \frac{dp}{p}$$

Calculate the fugacity of ethane at 104.4°C and 60 atm on the basis of the equation found if its compression factors are:

p , atm	13.61	27.22	40.82	54.43	68.04
Z	0.9508	0.8999	0.8476	0.7939	0.7394

Compare the result with the calculations by Eq. (4.16).

8. The temperature dependence of the saturated vapour pressure over liquid n -butane within the interval from -0.5 to $+75^\circ\text{C}$ is expressed by the equation

$$\log p = 4.11248 - \frac{1030.34}{251.041 + t}$$

Find the fugacity of n -butane at $t=16^\circ\text{C}$ if the density of its saturated vapour at this temperature is 0.00490 g/cm³.

Is it possible to neglect the difference between the fugacity and the pressure of the saturated vapour if the assumed accuracy of the equation given in the initial conditions is about 1%?

9. The partial molar volumes of hydrogen at 0°C for a mixture containing 60% hydrogen and 40% nitrogen are as follows:

p , atm	50	100	200	300	400
\bar{V}_{H_2} , cm ³	466.4	241.3	129.1	91.1	72.5

Calculate the fugacity of hydrogen in the mixture at $p=400$ atm with the aid of Eq. (4.18).

4.3. HEAT CAPACITY

The pressure dependence of the heat capacity is expressed by the equation

$$C_p = C_p^\circ - T \int_{p^\circ}^p \left(\frac{\partial^2 V}{\partial T^2} \right)_p dp = C_p^\circ + T \int_{p^\circ}^p \left(\frac{\partial^2 \alpha}{\partial T^2} \right)_p dp \quad (4.20)$$

where C_p° is the heat capacity at such a low pressure p° at which a gas may be considered as ideal and the heat capacity as independent of the pressure.

The integral in Eq. (4.20) is determined on the basis of a p - V - T relationship according to experimental data or with the aid of such an equation of state that will make it possible to obtain sufficiently accurate values of the second derivatives of V with respect to T .

If the values of the enthalpy at high temperatures are known, the heat capacity can be found using the equation

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (4.21)$$

The heat capacity can also be calculated by integration of the equation

$$\left(\frac{\partial C_p}{\partial p} \right)_T = -\mu \left(\frac{\partial C_p}{\partial T} \right)_p - C_p \left(\frac{\partial \mu}{\partial T} \right)_p \quad (4.22)$$

where μ is the Joule-Thomson coefficient (Sec. 4.5).

The calculation of the heat capacity of real gases is also considered in Sec. 6.1.

Examples

1. Show that with observance of Eq. (4.1), the pressure dependence of C_p according to Eq. (4.20) will become

$$C_p = C_p^\circ + \frac{2a}{RT^2} p - \frac{3ab}{R^2 T^3} p^2$$

What conclusions can be made from an analysis of this equation?

Solution. It follows from Eq. (4.1) that

$$V = \frac{RT}{p} - \frac{a}{pV} + \frac{ab}{pV^2} + b \approx \frac{RT}{p} - \frac{a}{RT} + \frac{abp}{R^2 T^2} + b$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} + \frac{a}{RT^2} - \frac{2abp}{R^2 T^3}$$

Hence

$$\left(\frac{\partial^2 V}{\partial T^2} \right)_p = -\frac{2a}{RT^3} + \frac{6abp}{R^2 T^4}$$

and in accordance with Eq. (4.20)

$$C_p = C_p^\circ - T \int_{p^\circ}^p \left(\frac{-2a}{RT^3} + \frac{6abp}{R^2 T^4} \right) dp = C_p^\circ + \int_{p^\circ}^p \frac{2a}{RT^2} dp - \int_{p^\circ}^p \frac{6abp}{R^2 T^3} dp$$

Considering that $p^\circ = 0$, we finally get

$$C_p \approx C_p^\circ + \frac{2a}{RT^2} p - \frac{3ab}{R^2 T^3} p^2$$

It follows from this equation that (a) at high temperatures and low pressures the heat capacity grows with the pressure approximately linearly; (b) at high pressures the last term is great, and for this reason the curve $C_p = f(p)$ passes through a maximum which is especially strongly marked at low temperatures.

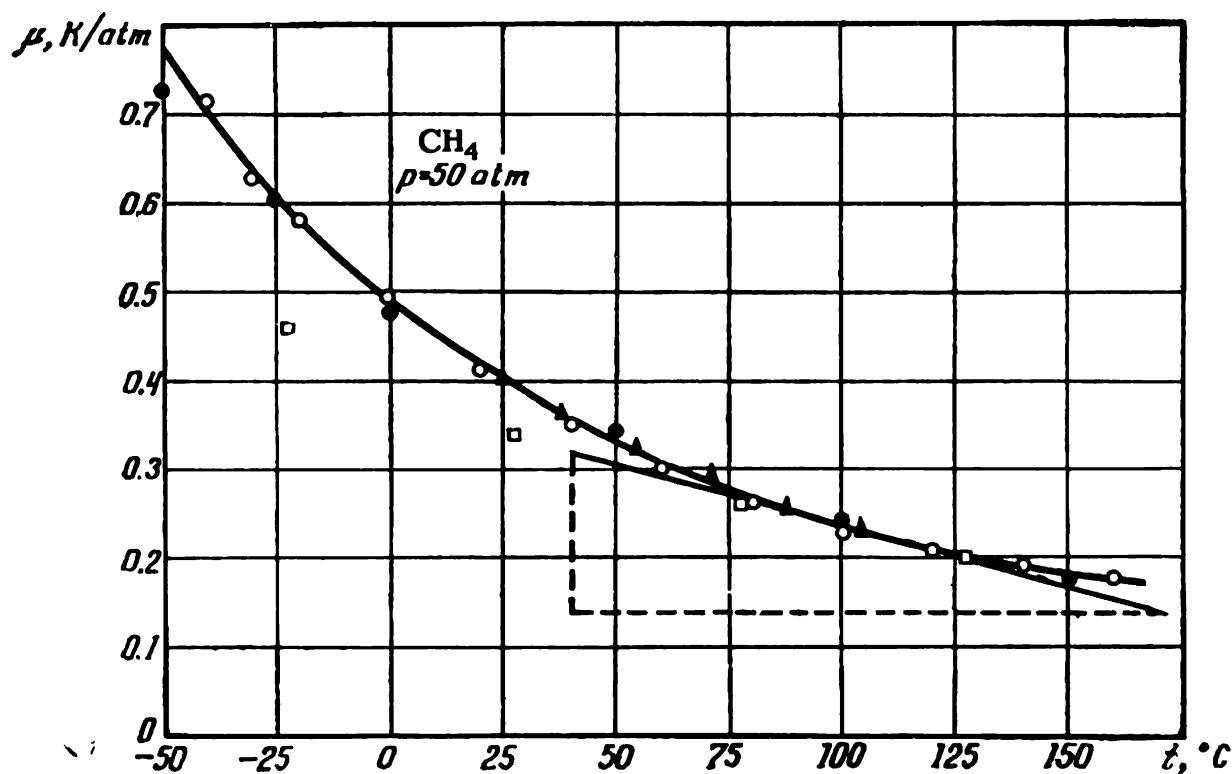


Fig. 16

2. Figure 16 gives experimental and calculated values of the Joule-Thomson coefficient μ for methane at $p=50$ atm and various temperatures.

Using the equation

$$C_p^\circ = 3.4 + 19.5 \times 10^{-3}T - 50.6 \times 10^{-7}T^2$$

find the value of $(\partial C_p / \partial p)_T$ at $t=100^\circ\text{C}$ and, assuming a linear dependence of C_p on p (at $T=\text{const}$), calculate C_p at $p=50$ atm and $t=100^\circ\text{C}$.

Compare the result with the value of $C_p=10.1$ cal/mol·K found by the processing of experimental data on the compressibility of methane.

Solution. We use Eq. (4.22) for the calculations.

At $t=100^\circ\text{C}$ we have

$$\begin{aligned} C_p^\circ &= 3.4 + 19.5 \times 10^{-3} \times 373.2 - 50.6 \times 10^{-7} \times 373.2^2 = \\ &= 9.97 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

$$\left(\frac{\partial C_p^\circ}{\partial T} \right)_p = 19.5 \times 10^{-3} - 101.2 \times 10^{-7} \times 373.2 = 15.72 \times 10^{-3}$$

According to Fig. 16 we find for $t=100^\circ\text{C}$ that $\mu\approx 0.235$ and $(\partial\mu/\partial T)_p = -0.001385$. Consequently,

$$\left(\frac{\partial C_p^\circ}{\partial p}\right)_T = -0.235 \times 15.72 \times 10^{-3} - 9.97(-0.001385) = 0.0101$$

or after integration on the assumption that the pressure dependence of C_p is linear, we get

$$C_p = C_p^\circ + 0.0101p \approx 9.97 + 0.5 = 10.47 \text{ cal/mol}\cdot\text{K}$$

This result differs from the one indicated in the initial conditions of the example by 3.7%.

Problems

1. Prove that if Eq. (4.1) holds for a gas, then the general equation

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_p$$

(see Problem 6 of Sec. 3.1) acquires the form

$$C_p - C_v \approx R + \frac{2a}{RT^2} p$$

What conclusions can be made from this equation?

2. Show that for a gas for which Eq. (4.2) holds, Eq. (4.20) becomes

$$C_p \approx C_p^\circ + \frac{81}{32} \frac{RT_{\text{cr}}^3}{p_{\text{cr}}T^3} p$$

Using the derived equation, find C_p° for gaseous *n*-pentane at $t=100^\circ\text{C}$ if $C_{p=1} = 34.7 \pm 0.2 \text{ cal/mol}\cdot\text{K}$. Take the values of t_{cr} and p_{cr} from Appendix 8.

Is it possible in the given case to neglect the difference between $C_{p=1}$ and C_p° ?

3. Find the molar heat capacity of methane at $t=100^\circ\text{C}$ and $p=100 \text{ atm}$.

Perform the calculations:

- (1) according to the equation derived in solving Example 1;
- (2) according to the equation derived in solving Example 2.

Take the temperature dependence of C_p° from the initial conditions of Example 2, and the constants of Eq. (4.1) and the values of t_{cr} and p_{cr} from Appendices 7 and 8, respectively.

Compare the result of the calculations with the value of $C_p=10.8$ found by the processing of experimental data.

4. Find the difference between C_p and C_v for methane at 100°C and 50 atm . Take the data required for the calculations from Appendix 7.

Perform the calculations with the aid of the equation derived in solving Problem 1.

Compare the results of the calculations with the value of 2.6 cal/K·mol obtained from experimental data.

5. If equation (4.3) is used to determine $(\partial^2 V / \partial T^2)_p$, then Eq. (4.20) after a certain simplification becomes transformed into the approximate formula

$$C_p = C_p^\circ + \left[\frac{2A_0}{RT^2} + \frac{12c}{T^4} \right] p$$

where A_0 and c are constants of Eq. (4.3).

Use this equation to calculate C_p for methane at $t=100^\circ\text{C}$ and $p=100$ atm if $A_0=2.2769$ and $c=12.83 \times 10^4$ for it ($R=0.08206$) and $C_p^\circ=9.6$ cal/mol·K.

Compare the result with the value of $C_p=10.8$ cal/mol·K found by the processing of experimental data.

6. The volume dependence of C_V in an isothermal process is expressed by the equation

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_V$$

(see Example 3, Sec. 3.1).

Prove that when Eq. (4.1) is observed, the isochoric heat capacity at $T=\text{const}$ does not depend on the volume.

7. May Eq. (4.4)

$$pV = A + Bp + CT$$

be used to calculate the pressure dependence of C_p ?

8. The temperature dependence of the enthalpy of superheated steam at $p=120$ kgf/cm² is given below:

$t, ^\circ\text{C} \dots$	330	340	350	360	370	380	390	400
$H, \text{kcal/kg}$	654.0	668.9	681.3	692.5	702.7	712.1	720.9	729.2

Find C_p for steam at $p=120$ kgf/cm² and $t=352^\circ\text{C}$. Compare the result of the solution with the experimentally obtained value equal to 1.2 kcal/kg·K.

9. Find $(\partial C_p / \partial p)_T$ for air at $T=300$ K if the temperature dependences of the Joule-Thomson coefficient and the heat capacity are expressed by the equations

$$\mu = -0.1975 + \frac{138.3}{T} - \frac{319.0}{T^2} \text{ and}$$

$$C_p \approx 6.50 + 0.001 T$$

4.4. ENTHALPY

The enthalpy is computed by the equation

$$H - H^0 = \int_{T^0}^T C_p dT + \int_{p^0}^p \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dp \quad (4.23)$$

where H^0 is the value of the enthalpy at a certain value of p^0 and T^0 , for example at $t=0^\circ\text{C}$ and $p=1$ atm.

The second term of the right-hand part of Eq. (4.23) accounting for the influence of the pressure on the enthalpy is determined on the basis of the p - V - T relationship according to experimental data or with the aid of an equation of state. If the calculations are based on the quantities Z (4.5) or μ (4.26), then Eq. (4.23) acquires the following form:

$$H - H^0 = \int_{T^0}^T C_p dT - \int_{p^0}^p \left(\frac{\partial Z}{\partial T} \right)_p \frac{RT^2}{p} dp \quad (4.24)$$

and

$$H - H^0 = \int_{T^0}^T C_p dT - \int_{p^0}^p (\mu C_p) dp \quad (4.25)$$

Successive calculations by Eqs. (4.24) and (4.25) permit the accuracy of the experimental data to be checked. The calculation of the enthalpy of real gases is also considered in Sec. 6.1.

Examples

1. Find the change in the enthalpy when one mole of methane is transferred from the state $p^0=1$ atm and $t^0=0^\circ\text{C}$ to the state $p=200$ atm and $t=200^\circ\text{C}$. Use the following data for the calculations: at $p=1$ atm

$t, ^\circ\text{C}$	0	50	100	150	200
$C_p, \text{ cal/g}\cdot\text{K}$	0.514	0.562	0.609	0.653	0.696

at $t=200^\circ\text{C}$

$p, \text{ atm}$	10	40	60	100	140	160	180	200
$V, \text{ cm}^3$	3879	968	644.7	388.0	279.2	245.2	219.3	198.6
$T/V \cdot (\partial V / \partial T)_p$	1.016	1.060	1.088	1.135	1.171	1.182	1.191	1.176

Solution. In accordance with the data given in the initial conditions of the example, we find the change in the enthalpy due to the growth in the temperature at a low pressure, and the change in the enthalpy due to the growth in the pressure at an elevated temperature. Owing to the independence of the change in a property on the path of a process, the total change in the enthalpy is equal to the sought value.

Since in the given case we have a linear change in C_p with a change in t , it is the simplest to determine the first term of the right-hand part of Eq. (4.23) analytically. According to the data given in the initial conditions, we have

$$\int_0^{200} C_p dt = \frac{0.514 + 0.696}{2} \times 200 \times 16.04 = 1941 \text{ cal/mol}$$

We find the second term of Eq. (4.23) with the aid of a chart (Fig. 17) of $V \left[1 - \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right]$ versus p

$$\int_1^{200} V \left[1 - \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right] dp = -10\,300 \text{ cm}^3 \cdot \text{atm} (= -249 \text{ cal/mol})$$

Consequently,

$$\Delta H = 1941 + (-249) = 1692 \text{ cal}$$

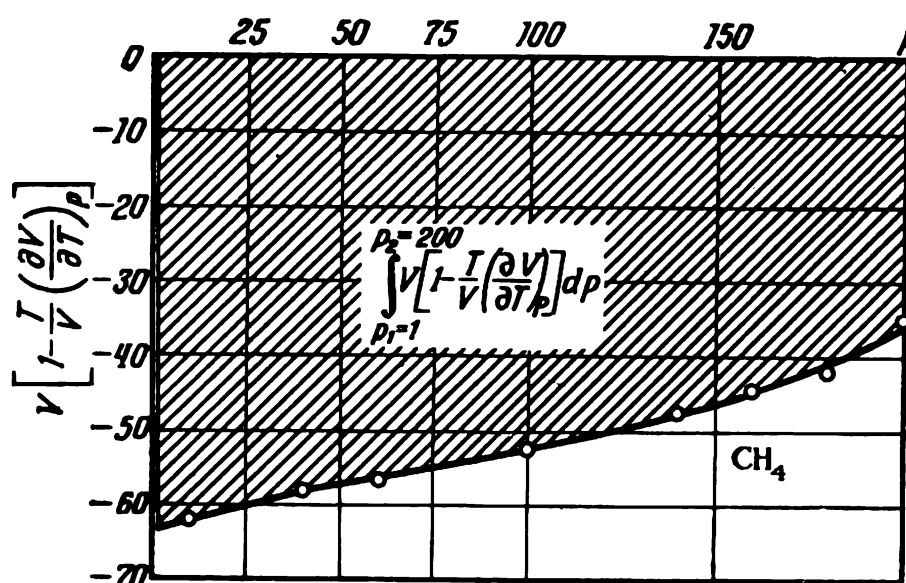


Fig. 17

2. Prove that the pressure dependence of the enthalpy for a gas which Eq. (4.2) holds for is expressed by the equation

$$H_2 - H_1 = \frac{9}{128} \frac{RT_{\text{cr}}}{p_{\text{cr}}} \left(1 - 18 \frac{T_{\text{cr}}^2}{T^2} \right) (p_2 - p_1)$$

Solution. Since the pressure dependence of the enthalpy is expressed by the equation

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p$$

(see Problem 5, Sec. 3.1), it is necessary to determine the values of V and $T(\partial V/\partial T)_p$. For this purpose we rewrite Eq. (4.2) in the form

$$V = \frac{RT}{p} \left[1 + \frac{9}{128} \frac{pT_{\text{cr}}}{T} \left(1 - 6 \frac{T_{\text{cr}}^2}{T^2} \right) \right] = \frac{RT}{p} + \frac{9RT_{\text{cr}}}{128p_{\text{cr}}} \left(1 - 6 \frac{T_{\text{cr}}^2}{T^2} \right)$$

or

$$V = \frac{RT}{p} + \frac{9}{128} \frac{RT_{\text{cr}}}{p_{\text{cr}}} - \frac{54}{128} \frac{RT_{\text{cr}}^3}{p_{\text{cr}}T^2}$$

whence

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{108}{128} \frac{RT_{\text{cr}}^3}{p_{\text{cr}} T^3}$$

$$T \left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{p} + \frac{108}{128} \frac{RT_{\text{cr}}^3}{p_{\text{cr}} T^2}$$

Consequently,

$$\begin{aligned} \left(\frac{\partial H}{\partial p}\right)_T &= V - T \left(\frac{\partial V}{\partial T}\right)_p = \frac{RT}{p} + \frac{9}{128} \frac{RT_{\text{cr}}}{p_{\text{cr}}} - \frac{54}{128} \frac{RT_{\text{cr}}^3}{p_{\text{cr}} T^2} - \frac{RT}{p} - \frac{108}{128} \frac{RT_{\text{cr}}^3}{p_{\text{cr}} T^2} = \\ &= \frac{9}{128} \frac{RT_{\text{cr}}}{p_{\text{cr}}} \left(1 - 6 \frac{T_{\text{cr}}^2}{T^2} - 12 \frac{T_{\text{cr}}^2}{T^2}\right) = \frac{9}{128} \frac{RT_{\text{cr}}}{p_{\text{cr}}} \left(1 - 18 \frac{T_{\text{cr}}^2}{T^2}\right) \end{aligned}$$

Integration of this equation gives the sought expression.

3. Figure 18 shows the temperature dependence of the compression factors for ethane at various pressures (the mean values from available experimental data).

Find the change in the enthalpy upon the isothermal compression of a mole of ethane from $p_1=17$ to $p_2=68$ atm if $t=104.4^\circ\text{C}$.

Compare the result of the calculations with the values of $H_{p=17.01}=113.30$ cal/g and $H_{p=68.04}=95.36$ cal/g found from the temperature dependence of the heat capacity.

Solution. We draw tangents to the points on the isobars where $t=104.4^\circ\text{C}$ and determine $(\partial Z/\partial T)_p$. We get the following results:

p , atm	13.6	34.0	54.4	68.0
$(\partial Z/\partial T)_p \times 10^3$	0.467	1.24	2.26	2.91
$(\partial Z/\partial T)_p RT^2/p$	9.73	10.2	11.8	12.1

Next we plot $(\partial Z/\partial T)_p RT^2/p$ versus p (Fig. 19). In accordance with Eq. (4.24) the sought quantity is determined by the area limited by the ordinates $p_1=17$ and $p_2=68$, the axis of abscissas and the plotted straight line. This area is equivalent to $\Delta H \approx 560$ cal.

The result obtained well agrees with the value given in the initial conditions of the example, since $(113.30 - 95.36) \times 30.07 = 539$ cal.

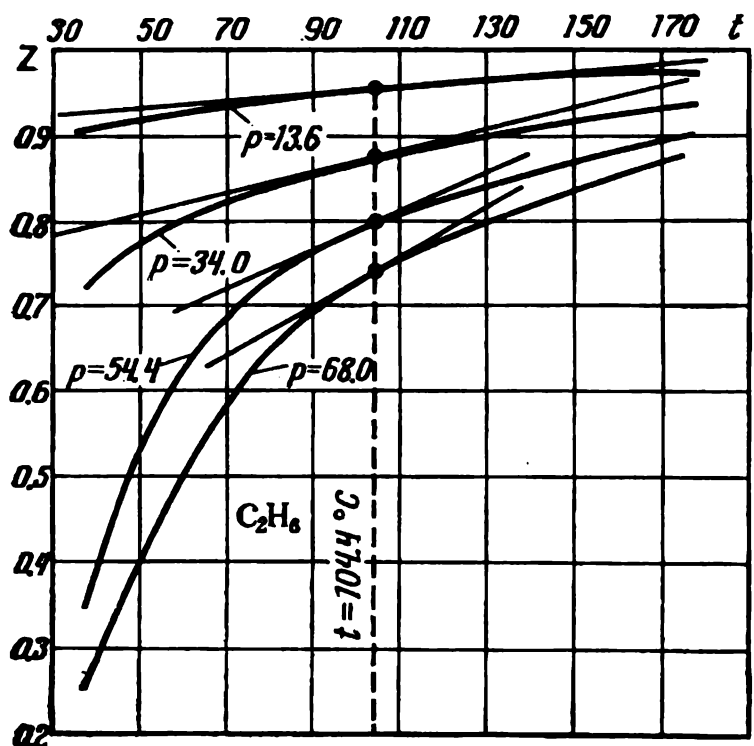


Fig. 18

Problems

1. Use Eq. (4.23) to derive an equation for calculating the change in the enthalpy upon the isothermal compression of a gas if Eq. (4.1) holds for it.

2. Calculate the change in the molar enthalpy of ammonia upon its expansion from $p_1=1$ atm to an infinitely small pressure (when the gas behaves like an ideal one) at $t=20^\circ\text{C}$ with the aid of the equation

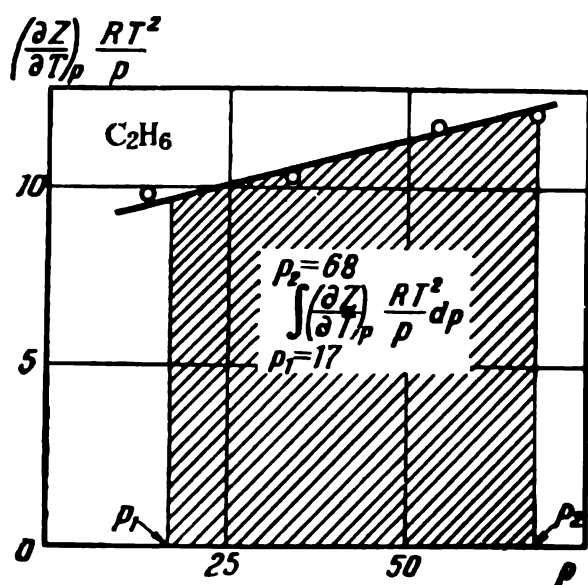


Fig. 19

derived when solving Example 2. Take the values of t_{cr} and p_{cr} from Appendix 8.

Is it possible to neglect the found value if the accuracy of processing the experimental data used to compute the enthalpy of ammonia at high pressures (over 100 atm) is estimated to be 1-3%, and the value of H at $t=200^\circ\text{C}$ and $p=20$ atm (the pressure beginning from which the calculations were performed) differs from that at $p=1$ by 134 cal?

3. Use Eq. (4.23) to show the truth of Eq. (4.24).

4. Find the change in enthalpy when ammonia is compressed from $p_1=20$ to $p_2=200$ atm if $t=200^\circ\text{C}$. Use the values of the molar volume of ammonia at different pressures and temperatures given in Table 9 for the calculations.

Table 9

$p, \text{ atm}$									
$t, ^\circ\text{C}$	20	40	60	80	100	125	150	175	200
150	1633	760.7	468.1	319.4	226.7	150.2	66.40	51.66	46.88
175	1752	831.2	522.2	366.6	271.7	194.0	139.7	93.30	72.94
200	1866	892.7	570.8	408.2	310.9	231.6	176.7	136.7	107.4
225	1978	956.7	616.1	445.5	342.9	260.4	204.7	164.9	135.1
250	2089	1016	659.1	480.3	373.2	287.1	229.2	193.5	157.1

5. Calculate the change in the enthalpy upon the isothermal compression of one mole of isobutane ($t=87.8^\circ\text{C}$) from $p_1=0$ to $p_2=15$ atm in accordance with the following values of the Joule-Thomson coefficient and the heat capacity for isobutane at $t=87.8^\circ\text{C}$:

$p, \text{ atm}$	0	1	2.72	5.44	8.51	11.91	15.31
$\mu, \text{ K/atm}$	0.60	0.76	1.00	1.31	1.56	1.76	1.90
$C_p, \text{ cal/mol}\cdot\text{K}$	0.4293	0.4332	0.4406	0.4542	0.4735	0.5019	0.5431

4.5. JOULE-THOMSON EFFECT

The *Joule-Thomson coefficient* is determined by the equation

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H = \frac{T (\partial V / \partial T)_p - V}{C_p} \quad (4.26)$$

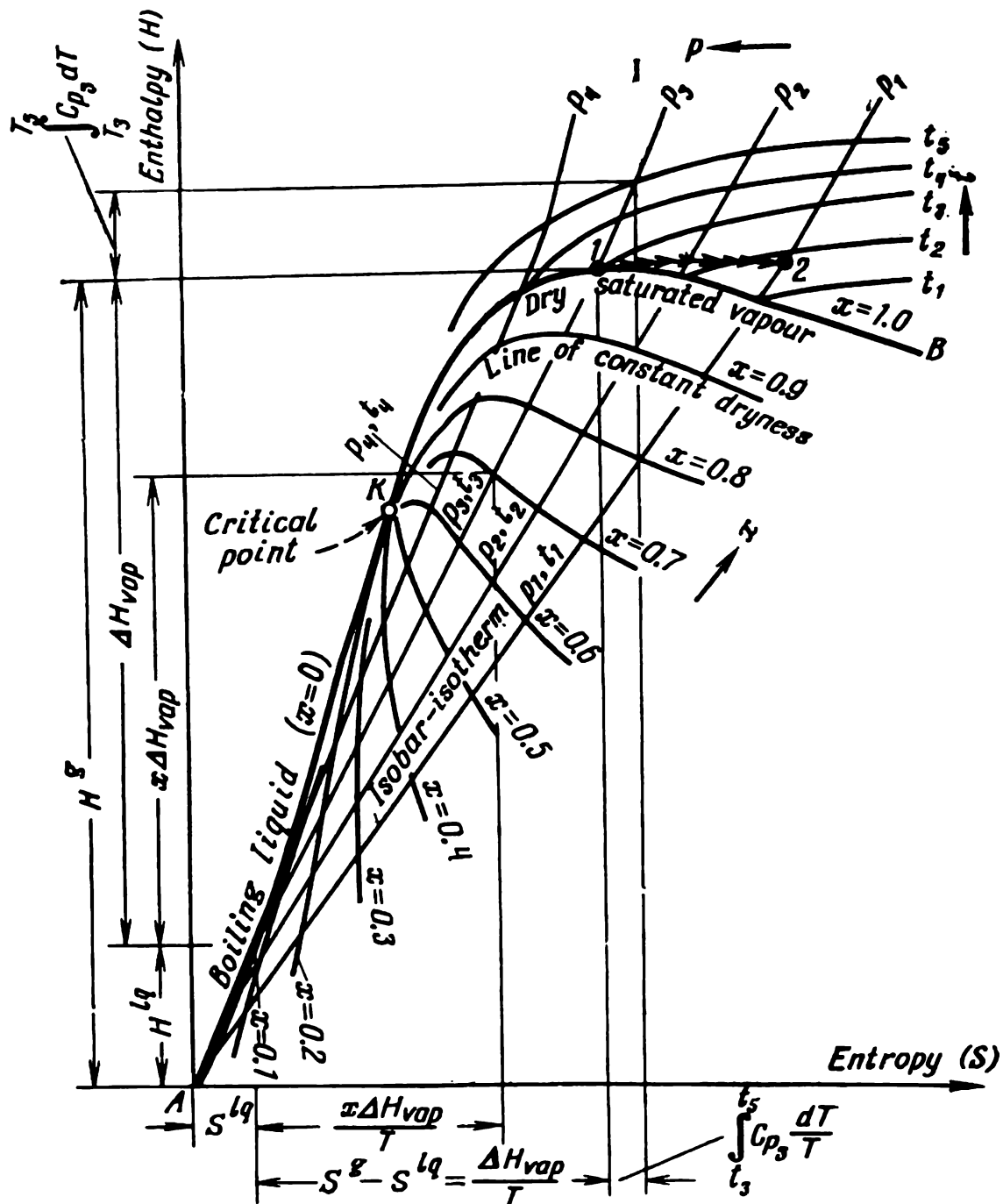


Fig. 20

The numerator of its right-hand part is determined either with the aid of experimental data on compressibility, or according to the corresponding equation of state.

At the *inversion point* (T_{inv} and p_{inv}) the Joule-Thomson coefficient reverses its sign.

Equation (4.26) can be written as follows:

$$\mu = \frac{1}{C_p} \left(\frac{\partial H}{\partial p} \right)_T \quad (4.27)$$

or

$$\mu = - \frac{RT^2}{C_p p} \left(\frac{\partial Z}{\partial T} \right)_p \quad (4.28)$$

The following equation is also used for calculations:

$$\left(\frac{\partial \mu}{\partial T} \right)_p = - \left(\frac{\partial \ln C_p}{\partial p} \right)_T - \mu \left(\frac{\partial \ln C_p}{\partial T} \right)_p \quad (4.29)$$

The integral of the Joule-Thomson coefficient

$$\Delta T = \int_{p_1}^{p_2} \mu dp$$

is usually determined graphically with the aid of an H - S diagram (Fig. 20) or a T - S diagram (Fig. 21) on the basis of the condition that $H_1 = H_2$ according to the quantities p_1 , t_1 and p_2 (line 1-2 in Figs. 20 and 21). In addition, tables of thermodynamic properties may be used, as well as direct integration of the pressure dependence of μ (graphical or analytical).

The calculations of the Joule-Thomson effect are also treated in Sec. 6.1.

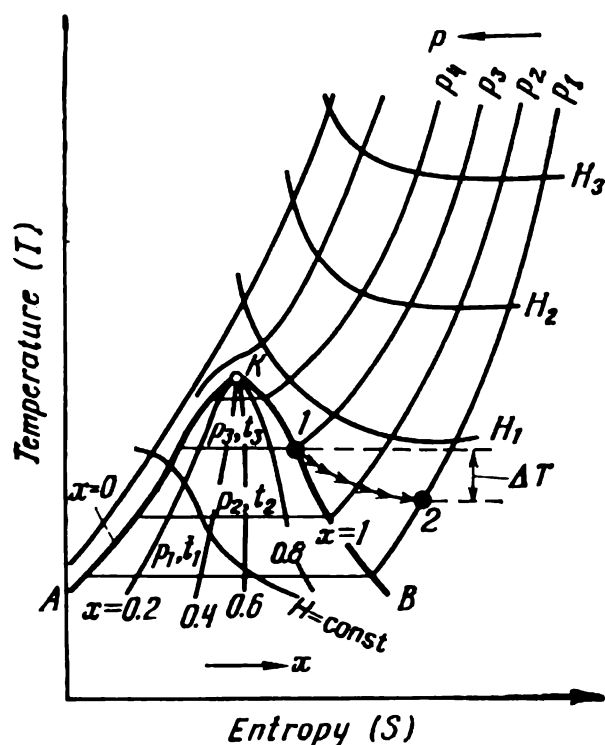


Fig. 21

Examples

1. The heat capacity of ammonia at $p=200$ atm and $t=225^\circ\text{C}$ is $C_p=20.5$ cal/K.

The temperature dependence of the molar volume for ammonia at $p=200$ is expressed by the following data:

$t, ^\circ\text{C}$	175	200	225	250	275
V, cm^3	72.94	107.4	135.1	157.1	176.8

Find the Joule-Thomson coefficient at $t=225^\circ\text{C}$.

Solution. According to the data given in the initial conditions we plot an isobar $V=f(T)$ and by graphical differentiation we find that at $t=225^\circ\text{C}$ we have $(\partial V/\partial T)_p=1$. Hence in accordance with Eq. (4.26)

$$\mu = \frac{498.2 \times 1 - 135.1}{20.5 \times 41.29} = 0.429 \text{ K/atm}$$

2. Show that for a gas for which Eq. (4.1) holds, Eq. (4.26) becomes

$$\mu \approx \frac{(2a/RT) - b - (3abp/RT^2)}{C_p}$$

How can the latter equation be simplified for low pressures and high temperatures?

Solution. It follows from Eq. (4.1) that

$$T \left(\frac{\partial V}{\partial T} \right)_p = V - b + \frac{2a}{RT} - \frac{3abp}{R^2 T^2}$$

and

$$T \left(\frac{\partial V}{\partial T} \right)_p - V \approx \frac{2a}{RT} - b - \frac{3abp}{R^2 T^2}$$

Hence

$$\mu \approx \frac{(2a/RT) - b - (3abp/R^2 T^2)}{C_p}$$

For a low pressure and high temperature, we can assume that $3abp/R^2 T^2 \approx 0$. Hence

$$\mu \approx \frac{(2a/RT) - b}{C_p}$$

3. Using Eq. (4.26) and assuming that $C_p = \text{const}$ and $\mu = a/T^n$ (where a and n are constants), prove that the equation of state of a real gas has the form

$$V = \frac{RT}{p} - \frac{aC_p}{(n+1)T^n}$$

In solving the equation use the circumstance that a gas approaches the state of an ideal one at $T_{p=\text{const}} \rightarrow \infty$.

Solution. Using the values of C_p and μ given above in Eq. (4.26), we get

$$\frac{aC_p}{T^n} = T \left(\frac{\partial V}{\partial T} \right)_p - V$$

Let us divide both parts by T^2 . Hence

$$\frac{aC_p}{T^{n+2}} = \frac{T(\partial V/\partial T) - V}{T^2} = \frac{\partial}{\partial T} \left(\frac{V}{T} \right)_p$$

or

$$\frac{V}{T} = -\frac{aC_p}{(n+1)T^{n+1}} + f(p) \quad (a)$$

Assuming that at $T_{p=\text{const}} \rightarrow \infty$ a gas becomes an ideal one, we have

$$\frac{V}{T} = \frac{R}{p}$$

whence

$$f(p) = \frac{R}{p}$$

Therefore in accordance with Eq. (a) we get the sought equation.

4. Saturated steam at $t=200^\circ\text{C}$ is throttled to $p=2\text{ kgf/cm}^2$.

Find the integral of the Joule-Thomson coefficient and the change in entropy in throttling. Perform the calculations:

(1) with the aid of an H - S diagram for H_2O ;

(2) according to tables of the thermodynamic properties of water and steam*.

Solution. 1. According to an H - S diagram for water and steam (see water property tables) we find the position of point 1 ($p \approx 16\text{ kgf/cm}^2$) (see the diagram in Fig. 20) and draw a horizontal line ($H \approx 667\text{ kcal/kg}$) through it up to the intersection with the isobar $p=2\text{ kgf/cm}^2$. We get point 2 characterizing the final state. In the diagram we find the temperature $t_2 \approx 160^\circ\text{C}$. Consequently, when the pressure drops from 16 to 2 kgf/cm^2 the temperature drops by 40 K .

The change in the entropy is

$$1.75 - 1.54 = 0.21\text{ kcal/kg} \cdot \text{K}$$

2. According to water property tables, the pressure of saturated steam at $t=200^\circ\text{C}$ is $p_1=15.857\text{ kgf/cm}^2$; we assume that $p_1 \approx 16$. Next we find the value of t_2 (corresponding to $p_2=2\text{ kgf/cm}^2$ and $H_2=667\text{ kcal/kg}$); it is equal to about 161°C . Consequently, the integral of the Joule-Thomson coefficient is 39 K . The change in the entropy is $\Delta S = 1.7548 - 1.5358 \approx 0.22\text{ cal/kg} \cdot \text{K}$.

Problems

1. Calculate the Joule-Thomson coefficient for methane at $p=50\text{ atm}$ and $t=100^\circ\text{C}$ and compare it with the experimental value equal to about 0.239 K/atm , if in these conditions V , $(T/V)(\partial V/\partial T)_p$ and C_p are respectively equal to 593.5 , 1.170 and 10.0 .

2. Using the equation derived in solving Example 2, find the Joule-Thomson coefficient for nitrogen at $p=60\text{ atm}$ and $t=25^\circ\text{C}$, if $C_p=7.6\text{ cal/mol} \cdot \text{K}$.

Compare the result with the experimental value equal to 0.169 .

3. What will the form of the equation of $\mu=f(p, T)$ for a nitrogen-hydrogen mixture (1 : 3) be if as a result of studying the heat capacity of the given mixture within the range from $t=25$ to 150°C and $p=1$ to 500 kgf/cm^2 the following equation was found for calculating the pres-

* In the following they will be called "water property tables" for purposes of brevity.

sure and temperature dependence of C_p :

$$C_p = 6.93 + 0.0004t + (260 - 0.76t) \times 10^{-5}p - \\ - (28.37 - 0.0874t) \times 10^{-7}p^2$$

4. Find the inversion point for nitrogen at $p=180$ atm. Use the equation derived in solving Example 2 for the calculations.

Compare the results of the calculations with the experimental data equal to -134.7 and 253°C .

5. If the equation of state (4.3) holds for a gas, then Eq. (4.26) can be transformed into the following approximate relationship:

$$\mu = \frac{\left(-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3}\right) + \left(\frac{2B_0b}{RT} - \frac{3A_0a}{R^2T^2} + \frac{5B_0c}{RT^4}\right)p}{C_p}$$

where A_0 , B_0 , a , b and c are constants of the equation of state (4.3).

Find the Joule-Thomson coefficient for nitrogen at $p=60$ atm and $t=25^\circ\text{C}$ if $C_p=7.6$ cal/mol·K and the constants of the equation are $A_0=1.3445$, $B_0=50.46 \times 10^{-3}$, $a=26.17 \times 10^{-3}$, $b=-6.91 \times 10^{-3}$, $c=4.20 \times 10^4$ and $R=0.08206$.

Compare the result of the calculations with experimental data and with the result of solving Problem 2.

6. Using the equation given in the initial conditions of Problem 5, find the inversion temperature of air at $p=140$ atm if the constants of Eq. (4.3) are $A_0=1.3012$, $B_0=46.11 \times 10^{-3}$, $a=19.31 \times 10^{-3}$, $b=-11.01 \times 10^{-3}$ and $c=4.34 \times 10^4$.

7. Find the change in the temperature in the throttling of moist steam with the aid of an H - S diagram (see water property tables) if $p_1=20$ kgf/cm², $p_2=1$ kgf/cm² and $t_2=120^\circ\text{C}$.

8. The Joule-Thomson coefficient for air at 0°C and different pressures has the following values:

p , atm.	1	20	60	100	140	180
μ , K/atm	0.2663	0.2443	0.2143	0.1782	0.1445	0.1125

Find the integral of the Joule-Thomson coefficient when the pressure drops from $p_1=150$ to $p_2=0$ atm. Compare the result of the calculations with the experimentally found value equal to about 36.7°C .

9. Show that for a gas for which Eq. (4.2) holds we have

$$\mu = \frac{9RT_{\text{cr}}}{128p_{\text{cr}}C_p} \left(1 - 18 \frac{T_{\text{cr}}^2}{T^2}\right)$$

Chapter Five

ONE-COMPONENT HETEROGENEOUS SYSTEMS

5.1. CLAPEYRON-CLAUSIUS EQUATION

The condition for the equilibrium coexistence of two phases in a one-component system (a boiling liquid and a saturated vapour, a melting crystalline body and a solidifying liquid, a subliming crystalline body and a vapour in equilibrium with it, a mixture of two isomorphic modifications) is expressed by the *Clapeyron-Clausius equation*

$$\left(\frac{\partial p}{\partial T}\right)_{\text{eq}} = \frac{S'' - S'}{V'' - V'} = \frac{H'' - H'}{T(V'' - V')} = \frac{\Delta H_{\text{ph.tr}}}{T_{\text{ph.tr}} \Delta V_{\text{ph.tr}}} \quad (5.1)$$

where $(\partial p / \partial T)_{\text{eq}}$ = derivative characterizing the relationship between the pressure and temperature on the curve showing the equilibrium of the coexisting phases (in the following the subscript "eq" has been omitted)

V' and S' = volume and entropy of a substance in the initial phase

V'' and S'' = ditto in the forming phase

$\Delta H_{\text{ph.tr}} = H'' - H' = T_{\text{ph.tr}} \Delta S_{\text{ph.tr}}$ = heat of transformation of phase (') into phase (').

As a rule, $\Delta H_{\text{ph.tr}}$, V' , V'' , S' and S'' are related to 1 mole or to a unit of mass (1 g or 1 kg). The indicated quantities respectively correspond: (1) for boiling—to the change of the pressure of the saturated vapour with the temperature (the curve of the liquid-vapour equilibrium line), the heat of vaporization and the increase in the volume and entropy in vaporization; (2) for melting—to the change in the melting point with the pressure $(\partial t / \partial p)_{\text{eq}}$, the heat of fusion and the change in the volume and entropy in melting; (3) for sublimation—to the dependence of p on t on the crystalline body-vapour equilibrium curve, to the heat of sublimation and the increase in the volume and entropy in sublimation; (4) for the transformation of one crystalline modification into another—to the relationship between p and t with these phases in equilibrium, to the heat and the changes in the volume and entropy in the phase transition.

If it is possible to neglect the volume of a condensed phase (liquid or crystalline body) in comparison with the volume of the saturated vapour and consider that the vapour is described by the Mendelev-

Clapeyron equation, then Eq. (5.1) becomes

$$\frac{\partial p}{\partial T} = \frac{\Delta H \cdot p}{RT^2} \quad (5.2)$$

$$\frac{\partial \ln p}{\partial T} = \frac{\Delta H}{RT^2} \quad (5.2a)$$

or

$$\frac{\partial \ln p}{\partial (1/T)} = -\frac{\Delta H}{R} \quad (5.2b)$$

where ΔH is the molar heat of vaporization (or sublimation).

Assuming in the first approximation that ΔH is constant, after integration of Eq. (5.2b) we get

$$\ln p = -\frac{\Delta H}{RT} + \text{const} \quad (5.3)$$

or

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5.3a)$$

In approximate calculations, it is possible to use the value of the molar heat of vaporization at the normal boiling point found on the basis of *Trouton's rule*:

$$\frac{(\Delta H_{\text{vap}})_{\text{n. b. p.}}}{T_{\text{n. b. p.}}} \approx 21 \quad (5.4)$$

Sections 5.2 and 5.4 are devoted to some other methods of calculating the vapour pressure and heats of phase transitions. Methods of calculating the heats of fusion and vaporization are also considered in Chapter Seven.

Approximate methods of calculating properties on liquid-vapour equilibrium curves are dealt with in Sec. 6.2.

Examples

1. The change in the melting point of diphenylamine $(\text{C}_6\text{H}_5)_2\text{NH}$ when the pressure changes at this point (54°C) can be assumed to approximately equal 0.027 K/atm .

Find the molar heat of fusion of diphenylamine if melting is accompanied by an increase in the volume equal to $95.8 \text{ cm}^3/\text{kg}$.

Compare the result of the calculations with the experimentally found value of $\Delta H_f = 4270 \text{ cal/mol}$.

Solution. In accordance with Eq. (5.1)

$$\begin{aligned} \Delta H_{\text{fus}} &= T \Delta V \frac{\partial p}{\partial T} = 327.2 \times \frac{95.8 \times 169.2}{1000} \times \frac{1}{0.027} = \\ &= 196\,000 \text{ atm} \cdot \text{cm}^3/\text{mol} = \frac{196\,000}{41.293} = 4760 \text{ cal/mol} \end{aligned}$$

which differs from the experimental value by 11.5%.

2. Is it possible to assume for water at $t=100$ and 369°C that

$$\frac{\partial p}{\partial T} \approx \frac{\Delta p}{\Delta T}$$

(considering that $\Delta T=2$) if at the temperatures indicated the volume of saturated steam is respectively equal to 1.673 and 0.065 24 m^3/kg , and the volume of the boiling liquid is 0.001 043 5 and 0.002 18 m^3/kg ? The heats of vaporization are equal to 538.9 and 116.3 kcal/kg .

Use the following data taken from water property tables for the calculations:

$t, ^\circ\text{C}$	99	101	368	370
$p, \text{kgf}/\text{cm}^2$	0.9969	1.0707	209.60	214.68

Solution. At $t=100^\circ\text{C}$ we have

$$\frac{\partial p}{\partial T} = \frac{538.9 \times 18.016 \times 41.293}{373.16 \times \frac{(1.673 - 0.001\,043\,5) \times 10^6}{10^3} \times 18.016} = 0.035\,67$$

According to the data given above we have

$$\frac{\Delta p}{\Delta T} = \frac{1.0707 - 0.9969}{1.0332(101 - 99)} = \frac{0.0738}{2.0664} = 0.035\,72$$

The difference between the exact and the approximate values is 0.15%.

At $t=369^\circ\text{C}$ we have

$$\frac{\partial p}{\partial T} = \frac{116.3 \times 18.016 \times 41.293}{642.16 \times \frac{(0.065\,24 - 0.002\,18) \times 10^6 \times 18.016}{10^3}} = 2.444$$

According to the data given above we have

$$\frac{\Delta p}{\Delta T} = \frac{214.68 - 209.60}{(370 - 368) \times 1.0332} = \frac{5.08}{2.0664} = 2.459$$

The difference (0.61%) is due not to a growth in the curvature of the line $p=f(t)$ (since the temperature interval is very small), but to a lower accuracy of the experimental data.

Consequently, in both cases the accuracy of the substitution of $\Delta p/\Delta T$ (with $\Delta T=2$) for $\partial p/\partial T$ may be acknowledged as sufficiently satisfactory.

3. The dependence of t_b on p for chloroform is expressed by the curve shown in Fig. 22.

Find the heat of vaporization of chloroform at $t_1=16$ and $t_2=61^\circ\text{C}$ and compare the results with the experimental data equal respectively to 66 and 59.7 cal/g .

Solution. By connecting the points corresponding to the experimental data, we get a curve of p versus T . We find by graphical differen-

tiation that at $t=16^{\circ}\text{C}$

$$\frac{\partial p}{\partial T} = \frac{150}{25.5} = 5.88 \text{ mm/K}$$

In accordance with Eq. (5.2) we have

$$5.88 = \frac{\Delta H_{\text{vap}} \times 125}{1.987 \times 289.2^2}$$

whence

$$\begin{aligned} \Delta H_{\text{vap}} &= \frac{5.88 \times 1.987 \times 289.2^2}{125} = \\ &= 7817 \text{ (65.5 cal/g)} \end{aligned}$$

At $t=61^{\circ}\text{C}$

$$\frac{\partial p}{\partial T} = \frac{350}{14} = 25.0 \text{ mm/K}$$

or in accordance with Eq. (5.2)

$$25.0 = \frac{\Delta H_{\text{vap}} \times 760}{1.987 \times 334.2^2}$$

whence

$$\begin{aligned} \Delta H_{\text{vap}} &= \frac{25.0 \times 1.987 \times 334.2^2}{760} = \\ &= 7300 \text{ (61.1 cal/g)} \end{aligned}$$

Both values of ΔH_{vap} coincide with the experimental ones within the limits of the error of an experiment and graphical differentiation.

4. The following data were obtained in investigating the vapour pressure over niobium pentachloride:

$t, ^{\circ}\text{C}$	100	151	181	190.5	200.5	210.5	219.5
$p, \text{ mm Hg}$	0.74	13.2	85.7	148.4	215.8	331.2	489.3

Using a plot of $\log p$ versus T^{-1} , find ΔH_{subl} and the boiling point of niobium pentachloride. Compare the latter value with the experimental one ($240\text{--}241^{\circ}\text{C}$).

Solution. According to the data given above we calculate the values of $1/T$ and $\log p$ (the values of p are in mm Hg):

$\frac{1}{T} \times 10^5$	268	236	220	216	211	207	203
$\log p$	-0.131	1.121	1.933	2.171	2.334	2.520	2.690

We plot the values obtained on a chart showing $\log p$ versus $1/T$ (Fig. 23) and according to the slope obtained calculate ΔH_{subl} with

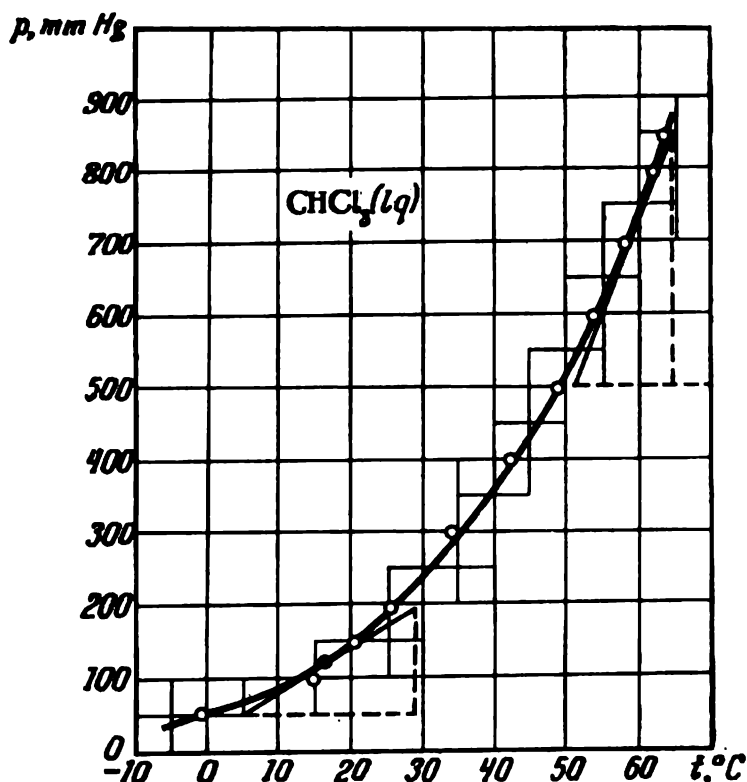


Fig. 22

the aid of Eq. (5.2b):

$$\Delta H_{\text{subl}}^* \approx -4.576 \times \frac{2.0 - 0}{0.00217 - 0.00264} = 19\,500 \text{ cal/mol}$$

To determine $T_{\text{n.b.p.}}$ we find in Fig. 23 the value of the abscissa corresponding to the value of the ordinate of $\log 760$ (2.88). We get

$$\frac{1}{T_{\text{n.b.p.}}} = 0.00198$$

or

$$T_{\text{n.b.p.}} = 505.1 \text{ K} \quad \text{and} \quad t = 232^\circ\text{C}$$

which differs from the value given in the initial conditions of the example by 8.9 K.

5. The pressure (in mm Hg) of the saturated vapour of mercury within the interval from 0 to 450 °C can be expressed by the equation

$$\log p = -\frac{3276.628}{T} -$$

$$-0.651\,990\,4 \log T + 9.907\,343\,6$$

Determine ΔH_{vap} at the normal boiling point (357 °C) and compare it with

the average of the values found experimentally, namely,

$$(\Delta H_{\text{vap}})_{\text{n.b.p.}} = \frac{15\,500 + 13\,600}{2} = 14\,550 \text{ cal/mol}$$

Solution. Multiplying both parts of the equation by 2.303 to pass over from common to natural logarithms, we get

$$\ln p = \frac{-3276.628 \times 2.303}{T} - 0.651\,990\,4 \ln T + 9.907\,343\,6 \times 2.303$$

whence

$$\frac{d \ln p}{dT} = \frac{3276.628 \times 2.303}{T^2} - \frac{0.651\,990\,4}{T}$$

or in accordance with Eq. (5.2a)

$$\frac{\Delta H_{\text{vap}}}{RT^2} = \frac{3276.628 \times 2.303}{T^2} - \frac{0.651\,990\,4}{T}$$

It follows from this equation that

$$\Delta H_{\text{vap}} = 1.987 \times 3276.628 \times 2.303 - 1.987 \times 0.651\,990\,4 \, T$$

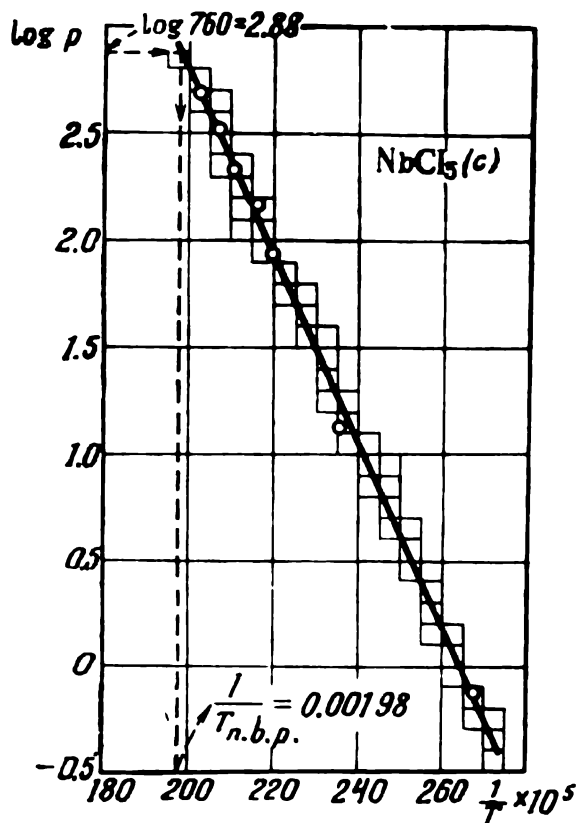


Fig. 23

hence

$$(\Delta H_{\text{vap}})_{\text{n. b. p.}} = 1.987 \times 3276.628 \times 2.303 - 1.987 \times \\ \times 0.6519904 \times 630.2 = 14190 \text{ cal/mol}$$

which differs from the value given in the initial conditions of the example by 360 cal (2.5%).

6. The vapour pressure of nickel carbonyl at $t=0$ and 13°C is respectively equal to 129 and 224 mm Hg.

Find Eq. (5.3) on the basis of these data, determine $t_{\text{n. b. p.}}$ and compare it with the experimentally found value (43°C).

Solution. Let us write Eq. (5.3) in the form

$$\log p = -\frac{A}{T} + B$$

In accordance with the data given in the initial conditions, we have

$$\log 129 = -\frac{A}{273.2} + B \quad \text{and} \quad \log 224 = -\frac{A}{286.2} + B$$

whence

$$2.35025 - 2.11059 = -\frac{A}{286.2} + \frac{A}{273.2}$$

or

$$0.23966 = \frac{13A}{286.2 \times 273.2}$$

Consequently

$$A = \frac{0.23966 \times 286.2 \times 273.2}{13} = 1442$$

We determine the integration constant B :

$$\log 129 = -\frac{1442}{273.2} + B$$

whence

$$B = 7.3888$$

Thus the sought equation will have the form

$$\log p = -\frac{1442}{T} + 7.3888$$

For $t_{\text{n. b. p.}}$ we get

$$\log 760 = 2.8808 = -\frac{1442}{T} + 7.3888$$

or

$$T_{\text{n. b. p.}} = \frac{1442}{4.508} = 319.9 \text{ K} \quad \text{and} \quad t = 46.7^\circ\text{C}$$

which differs from the value indicated in the initial conditions by 3.7 K.

7. The pressure of phosgene vapour at $t_1=9.91^\circ\text{C}$ is 804.1, and at $t_2=1.35^\circ\text{C}$ is 578.8 mm Hg.

Calculate the heat of vaporization and compare it with the experimental value for the interval from 2.7 to 140°C equal to about 57.7 cal/g.

Solution. In accordance with Eq. (5.3a)

$$\log \frac{804.1}{578.8} = \frac{\Delta H_{\text{vap}}}{4.576} \left(\frac{1}{274.5} - \frac{1}{283.1} \right)$$

whence

$$\Delta H_{\text{vap}} = \frac{0.14278 \times 4.576 \times 274.5 \times 283.1}{8.56} = 5.930 \text{ (59.9 cal/g)}$$

The discrepancy is 3.6%.

8. Find the boiling point of ethyl benzoate ($\text{C}_9\text{H}_{10}\text{O}_2$) at $p=200$ mm Hg if $t_{\text{n.b.p.}}=213^\circ\text{C}$ and $(\Delta H_{\text{vap}})_{\text{n.b.p.}}=10564$ cal/mol.

Reference books recommend the value of $t_{p=200 \text{ mm}}=164.8^\circ\text{C}$.

Solution. In accordance with Eq. (5.3a)

$$\log \frac{760}{200} = \frac{10564}{4.576} \left(\frac{1}{T_1} - \frac{1}{486.2} \right) \quad \text{or} \quad \frac{0.57978 \times 4.576 \times 486.2}{10564} = \frac{486.2 - T_1}{T_1}$$

or

$$0.1221 T_1 = 486.2 - T_1$$

Consequently

$$T_1 = \frac{486.2}{1.1221} = 433.3 \text{ K } (t = 160.1^\circ\text{C})$$

9. The heat of formation of formic acid at $t_{\text{n.b.p.}}=100.6^\circ\text{C}$ is 117.6 cal/g, and the heat of vaporization of ethyl alcohol at $t_{\text{n.b.p.}}=78.3^\circ\text{C}$ is 195.3 cal/g.

1. Find by how much these values deviate from the rule expressed by Eq. (5.4).

2. How can these deviations be explained?

Solution. 1. By Eq. (3.15)

$$(\Delta S_{\text{n.b.p.}})_{\text{HCOOH}} = \frac{117.6 \times 46.03}{100.6 + 273.2} = 14.5 \text{ cal/g} \cdot \text{K}$$

$$(\Delta S_{\text{n.b.p.}})_{\text{C}_2\text{H}_5\text{OH}} = \frac{195.3 \times 46.07}{78.3 + 273.2} = 25.6 \text{ cal/g} \cdot \text{K}$$

2. These results indicate that formic acid is associated in its vapours (for this reason the heat of association partly compensates for the expenditure of energy for vaporization), while ethyl alcohol is associated in the liquid phase (this is why the consumption of heat for vaporization grows).

Problems

1. When heated, rhombic sulphur transforms into the monoclinic element; $\Delta V_{\text{ph.tr}} = 13.8 \text{ cm}^3/\text{kg}$. The transition point at $p = 1 \text{ atm}$ is 96.7°C , and its change with the pressure is determined by the factor $\partial t/\partial p = 0.033$.

Find the heat of transition.

Compare the result of the calculations with the value found according to the heats of combustion of rhombic and monoclinic sulphur equal respectively to $-70\,940$ and $-71\,020 \text{ cal/g-atom}$.

2. The pressure dependence of the melting point of naphthalene is expressed by the equation

$$t_{\text{fus}} = 80.1 + 376 \times 10^{-4}p - 192 \times 10^{-8}p^2$$

Find ΔH_{fus} at $p = 1 \text{ atm}$ if $\Delta V_{p=1} = 145.8 \text{ cm}^3/\text{kg}$.

Compare the result with the experimentally found value of $\Delta H_{\text{fus}} = 149.8 \text{ J/g}$.

3. It was found in one investigation that the heat of fusion of methane at $T_{\text{fus}} = 90.67 \text{ K}$ is 224 cal/mol . In another investigation it was established that the influence of the pressure on the melting point of methane within the interval from 1 to 200 atm is expressed by the equation

$$T_{\text{fus}} = 90.667 + 2.635 \times 10^{-2}p - 6.23 \times 10^{-6}p^2$$

and the change in volume in melting is $2.69 \text{ cm}^3/\text{mol}$. Do these data agree with each other?

4. Is it possible to melt 10 kg of tin in a crucible with a volume of 1.4 dm^3 if its heat of fusion is 14.2 cal/g , $t_{\text{fus}} = 232^\circ\text{C}$, $\rho^c = 7.18 \text{ g/cm}^3$ and $\partial T/\partial p \approx 0.0033$?

5. For white phosphorus the pressure dependence of the melting point and the change in volume in melting is expressed by the following data:

$p, \text{ atm}$	1	1000	2000	3000	4000
$t_{\text{fus}}, ^\circ\text{C}$	44.2	73.8	101.0	126.8	151.3
$\Delta V, \text{ cm}^3/\text{kg}$	19.3	17.9	16.6	15.4	14.2

Find ΔH_{fus} at $p = 2500 \text{ atm}$ by graphical processing of the experimental data. May this quantity be considered as constant within the interval of $p = 1$ to 2500 atm if $(\Delta H_{\text{fus}}) = 155 \text{ cal/mol}$ at $p = 1 \text{ atm}$?

6. The melting point of anethole ($\text{CH}_3\text{CH}:\text{CHC}_6\text{H}_4\text{OCH}_3$) is 21.5°C , and $\Delta H_{\text{fus}} = 108 \text{ J/g}$. The change of volume in melting is $79.3 \text{ cm}^3/\text{kg}$ (at 74 atm).

Find the pressure at which the melting point will be 100°C . Assume the values of $\partial p/\partial T$ and ΔH to be constant. The experimentally found value is $p = 4050 \text{ atm}$.

7. The densities of boiling ethane and its saturated vapour at the normal boiling point (-88.6°C) are respectively 0.546 and $0.002\,06 \text{ g/cm}^3$.

Find $(\Delta H_{\text{vap}})_{\text{n.b.p.}}$, if the temperature dependence of the pressure (in mm Hg) of saturated ethane at temperatures close to T_{cr} can be expressed by the equation

$$\log p = 6.810\,82 - \frac{661.088}{256.504 + t}$$

Compare the results with the value $\Delta H_{\text{vap}} = 3514 \pm 4$ cal/mol found experimentally.

8. The temperature dependence of the pressure can be expressed by the equation

$$\log p = \frac{T - T_{\text{n.b.p.}}}{T} \left[A - B \frac{T - T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} + C \left(\frac{T - T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} \right)^2 \right]$$

where A , B and C are constants.

1. What form will Eq. (5.1) take on in the given case?
2. Find $(\Delta H_{\text{vap}})_{183.2}$ for ethylene if $T_{\text{n.b.p.}} = 169.3$ K, $\rho^{\text{lq}} = 0.549$ and $\rho^{\text{g}} = 0.0041$ g/cm³, and the constants of the equation of $p = f(T)$ are $A = 4.330$, $B = 0.59$ and $C = 0.70$.

9. Below are given some thermodynamic properties of Freon-113 (Cl₂FC—CFCl₂). The temperature dependence of the vapour pressure of this substance is expressed by the equation

$$\log p = 29.5335 - \frac{2406.10}{T} - 9.2635 \log T + 0.003\,697\,0T$$

and the densities of the coexisting phases by the following data:

$t, ^\circ\text{C}$	−34.44	−12.22	+5.56	43.33
$\rho^{\text{g}}, \text{g/cm}^3$	0.000 195	0.000 683	0.002 385	0.006 468
$\rho^{\text{lq}}, \text{g/cm}^3$	1.6921	1.6473	1.5866	1.5209
$t, ^\circ\text{C}$	71.11	98.89	124.12	154.4
$\rho^{\text{g}}, \text{g/cm}^3$	0.014 65	0.029 25	0.050 81	0.093 97
$\rho^{\text{lq}}, \text{g/cm}^3$	1.4501	1.3742	1.2985	1.1891
$t, ^\circ\text{C}$	177.2	192.4	203.2	209.3
$\rho^{\text{g}}, \text{g/cm}^3$	0.150	0.208	0.280	0.346
$\rho^{\text{lq}}, \text{g/cm}^3$	1.0836	0.9916	0.8964	0.8164

Find the heats of vaporization at all the temperatures listed above. Plot a chart of ΔH_{vap} versus T .

10. Using the data given in the initial conditions of Example 2 and found in solving it, determine the possibility of calculating ΔH_{vap} for water at 100 °C ($p = 1$ atm) and 369 °C ($p = 205.3$ atm) if (1) the volume of the liquid is neglected; (2) steam is assumed to be an ideal gas; and (3) the volume of the liquid is neglected and steam is considered to be an ideal gas.

11. Show with the aid of Eq. (5.1) that at low pressures the approximate value of ΔH_{fus} can be found by the equation

$$\Delta H_{\text{fus}} \approx \left[\left(\frac{\partial p}{\partial T} \right)_{\text{subl}} - \left(\frac{\partial p}{\partial T} \right)_{\text{vap}} \right] \frac{RT^2}{p}$$

Use this equation to calculate the heat of fusion of methane if the temperature dependence of the pressure can be expressed by the following equations (p is in mm Hg):

for crystalline methane

$$\log p = 6.30181 - \frac{320.303}{255.84 + t}$$

for liquid methane

$$\log p = 6.56430 - \frac{380.224}{264.804 + t}$$

$$(t_{\text{fus}} = -182.5^\circ\text{C})$$

Compare the result with the experimentally found value of $\Delta H_{\text{fus}} = 224$ cal/mol.

12. The following equation was proposed as a result of studying the temperature dependence of the vapour pressure of $\text{Hg}(\text{CH}_3)_2$ (lq):

$$\log p = \frac{11100}{T^2} - \frac{1050}{T} + 6.563 \quad (t = -60 \text{ to } 100^\circ\text{C})$$

Is it possible to use this equation for an approximate estimation of the temperature dependence of ΔH_{vap} ?

13. By the internal heat of vaporization is meant the quantity

$$\Delta U_{\text{vap}} = \Delta H_{\text{vap}} - p(V^g - V^{\text{lq}})$$

Show that

$$\frac{\Delta U_{\text{vap}}}{\Delta H_{\text{vap}}} = 1 - \frac{d \ln T}{d \ln p}$$

14. The heat of vaporization of octane at 125.7°C equals 70.4 cal/g. Find the change in the pressure of the saturated vapour with a change in the temperature (in mm Hg/K) near the normal boiling point, assuming that $\partial T = \Delta T = 1$ K and compare it with the value of 21.7 found by the equation

$$\frac{\partial p}{\partial T} \approx \frac{810 - 710}{t_{p=810} - t_{p=710}}$$

15. The following equation was proposed for the temperature dependence of ΔH_{vap} for methyl alcohol:

$$\frac{\Delta H_{\text{vap}}}{T} = 266.7 - 41.5 \ln T$$

Find the increase in the boiling point when the pressure grows by 1 mm at $t_{n.b.p.} = 64.7^\circ\text{C}$ and compare it with the approximate experimentally found value equal to 0.0321 K/mm.

16. For water at 100°C we have $H^g = 638.9$ and $H^{lq} = 100.04$ kcal/kg. May Eq. (5.2) be used for accurate calculations of the values of $\partial p/\partial T$ if the error in the values of the enthalpies does not exceed 0.3%?

17. Determine the consumption of heat in the process of isobaric heating ($p = 1$ atm) of 1 kg of hexane from $t_1 = 20$ to $t_2 = 100^\circ\text{C}$.

Use the following data for the calculations:

$$(C_p)_{C_6H_{14}}^{lq} (\text{cal/g}) = 0.4955 + 0.9362 \times 10^{-3}t$$

$$(C_p)_{C_6H_{14}}^g (\text{cal/g}) = 0.2929 + 1.0921 \times 10^{-3}t$$

$$\log p (\text{mm Hg}) = 7.1584 - \frac{1322.65}{240.40 + t}$$

18. The temperature dependence of the pressure (in mm Hg) of the saturated vapour over crystalline and liquid ammonia is expressed by the equations

$$\log p_{NH_3}^c = 10.00593 - \frac{1630.70}{T}$$

and

$$\log p_{NH_3}^{lq} = 11.83997 - \frac{1612.50}{T} - 0.012311T + 0.000012521T^2$$

respectively, the former equation being valid up to the triple point, and the latter from the triple point to 240 K.

(1) Determine the coordinates of the triple point.

(2) Find ΔH_{fus} at the triple point, considering the ammonia vapour to be an ideal gas.

Compare the result of the calculations with the reference value of $\Delta H_{fus} = 1352$ cal.

19. The temperature dependence of the vapour pressure of hydrogen within the interval from $p = 1$ to p_{cr} may be expressed by the following equation:

$$\log p = -\frac{56.605}{T} + 3.8015 - 0.10458T + 0.003321T^2 - 0.000032197T^3$$

At $t = -245.73^\circ\text{C}$ we have $\Delta H_{vap} = 89.71$ kcal/kg, $\rho^g = 0.00613$ kg/dm³ and $\rho^{lq} = 0.06050$ kg/dm³. Do these data agree with each other?

20. Find the molar entropy of liquid dimethyl acetylene at 25°C if its molar entropy in the vaporous state at $p = 1$ atm and $t = 25^\circ\text{C}$ equals 67.9 cal/mol·K, and the temperature dependence of the pressure (within the range from -30 to $+27.2^\circ\text{C}$) is expressed by the equation

$$\log p = 6.9567 - \frac{1050.57}{230.59 + t}$$

21. Investigation of the vapour pressure of nicotine ($C_{10}H_{14}N_2$) resulted in the following data:

$t, ^\circ C$	170	185	190	200	209	221	228
$p, \text{ mm Hg}$	100	160	180	240	300	400	500

Plot a chart of p versus t .

Use the chart to find ΔS_{vap} at $t=200^\circ C$.

22. The saturated vapour pressure of antimony trisulphide is expressed by the following data:

$t, ^\circ C$	795	834	844	853	856	869	952
$p, \text{ mm Hg}$	13	20	24	26	35	57	127

1. Smooth out the experimental data with the aid of a chart of $\log p$ versus T^{-1} .

2. Find the normal boiling point and compare it with the experimentally obtained value of $1080^\circ C$.

3. Determine the vapour pressure at $895^\circ C$.

23. The sublimation and boiling points of methane have the following values at different pressures

$p, \text{ mm Hg}$	1	5	10	20	40
$t, ^\circ C$	-205.40	-199.0	-195.5	-191.8	-187.7
$p, \text{ mm Hg}$	60	100	200	400	760
$t, ^\circ C$	-185.1	-181.4	-175.5	-168.8	-161.5

Using the plot of $\log p$ versus T^{-1} , find (1) the coordinates of the triple point (the melting point), and (2) the molar heats of sublimation, vaporization and melting.

Compare the results of the solution with the experimentally obtained data: (1) $t=-182.5^\circ C$ and $p=70 \text{ mm Hg}$, and (2) $\Delta H_{\text{fus}}=224 \text{ cal/mol}$.

24. On the basis of the temperature dependence of the vapour pressure of liquid bismuth given below, derive a linear equation of $\log p=f(T^{-1})$ (using the method of mean values):

$t, ^\circ C$	470	515	575	580	610	630	705
$p, \text{ mm Hg}$	0.000 158	0.000 521	0.004 92	0.005 02	0.012 03	0.020 4	0.083 2

Use the found equation to calculate ΔH_{vap} .

25. Show that if a vapour is an ideal gas, then

$$\ln \frac{p^c}{p^{lq}} = \Delta H_{\text{fus}} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right)$$

where p^c = vapour pressure of the crystalline substance at T

p^{lq} = vapour pressure of the supercooled liquid at T .

Find $(\Delta H_{\text{fus}})_{\text{CH}_4}$ with the aid of this equation and the chart plotted in solving Problem 23. Perform the calculations for $T=81.4 \text{ K}$. Compare the result with the tabulated value of $\Delta H_{\text{fus}}=224 \text{ cal/mol}$.

By how much will the result change if the temperature of the supercooled liquid is found by the equation (p is in mm Hg)

$$\log p = 6.56430 - \frac{380.224}{264.804 + t}$$

26. The normal boiling point of iodine is 185°C and $\Delta H_{\text{vap}} = 39.2 \text{ cal/g}$. What temperature should iodine be heated to in an apparatus in which a pressure of 100 mm Hg is maintained to ensure its distillation?

27. At what pressure will diethylamine boil at 20°C if the normal boiling point is 58°C and $(\Delta H_{\text{vap}}) = 6655 \text{ cal/mol}$?

28. The boiling point of liquid methanol at $p = 200 \text{ mm Hg}$ is 34.7°C , and at 400 mm Hg is 49.9°C .

Calculate the boiling point at normal pressure and compare it with the most authentic value of $t_{\text{n.b.p.}} = 64.7^\circ\text{C}$.

29. The vapour pressure of crystalline acetylene at 132 K is 1.7 mm Hg, and at 153 K is 27.6 mm Hg.

Find the heat of fusion of acetylene if its specific heat of vaporization is 197.9 cal/g .

30. The temperature dependence of the pressure (in mm Hg) of the saturated vapour of liquid arsenous anhydride is expressed by the equation

$$\log p = -\frac{6670}{T} + 13.278$$

the melting point is 313°C and $\Delta H_{\text{fus}} = 7719 \text{ cal}$.

Find the vapour pressure over the crystalline arsenous anhydride at 310°C with the aid of the equation derived in solving Problem 25 and compare it with the value of $p = 60 \text{ mm Hg}$ found experimentally.

31. The boiling point of diethyl ether at $p = 600 \text{ mm Hg}$ is $t = 29.21^\circ\text{C}$, and at 900 mm Hg it is 40.25°C .

May the quantity $\partial p / \partial T$ at the normal boiling point be taken equal to $\Delta p / \Delta T$ if it is considered that the error in measuring the vapour pressure does not exceed 1%?

32. What amount of air must be passed through carbon sulphide at $p = 720 \text{ mm Hg}$ and $t = 40^\circ\text{C}$ to extract 30 g of the carbon sulphide if ΔH_{vap} for the latter is 85.03 cal/g at $t_{\text{n.b.p.}} = 46.5^\circ\text{C}$?

33. Check the truth of Eq. (5.4) on the example of substances for which the values of $(\Delta H_{\text{vap}})_{\text{n.b.p.}}$ are known from the initial conditions and solutions of the preceding examples and problems of the present section, and find the numerical value of the constant (the arithmetical mean of all the values).

34. Show that if Eq. (5.4) holds, then Eq. (5.3) becomes

$$\log p = -\frac{(\Delta H_{\text{vap}})_{\text{n.b.p.}}}{4.576T} + 4.59$$

Check the truth of this equation on the example of *m*-xylene for which $t_{n.b.p.} = 139.1^\circ\text{C}$ if the saturated vapour pressure at $t = 110.2^\circ\text{C}$ equals 350 mm Hg.

35. Ethyl bromide boils at 44.01°C at a pressure of 900 mm Hg. Using the equation found in solving the preceding problem, determine $t_{n.b.p.}$.

Compare the result of the solution with the experimentally found value equal to 38.41°C .

36. The following equation has been proposed for the temperature dependence of the heat of vaporization of liquid sulphur dioxide

$$\frac{\Delta H_{\text{vap}}}{T} = 247 - 40.21 \ln T$$

May we consider that Eq. (5.4) holds for liquid sulphur dioxide if according to experimental data $t_{n.b.p.} = -10^\circ\text{C}$?

37. The normal boiling points for ethyl bromide, acetone and liquid hydrogen sulphide are respectively equal to 38.4 , -56.5 and -60.4°C .

The heating of which of these compounds at $t \approx t_{n.b.p.}$ will call forth the greatest increase in pressure?

38. Prove that if a vapour is considered to be an ideal gas, then for substances satisfying Eq. (5.4) the following laws are observed:

$$(1) \frac{\Delta H_{\text{vap}}}{V^g} \approx 0.256 \quad \text{and} \quad (2) T \frac{\partial p}{\partial T} \approx 10.6$$

5.2. METHODS FOR COMPARATIVE CALCULATION OF THE TEMPERATURE DEPENDENCE OF SATURATED VAPOUR PRESSURE

The methods for the comparative calculation are based on a comparison of the boiling points or the vapour pressures of different substances.

The boiling points can be found with the aid of the *Duhring equation*

$$T_2 = A_1 T_1 + B_1 \quad (5.5)$$

and the *Henglein equations*

$$\ln T_2 = A_2 \ln T_1 + B_2 \quad (5.6)$$

$$\frac{1}{T_2} = A_3 \frac{1}{T_1} + B_3 \quad (5.7)$$

(or the charts corresponding to them), where T_2 and T_1 are the boiling points of the substances being compared at equal vapour pressures.

The pressure of a saturated vapour can be determined by the *Kireev-Othmer equation*

$$\ln p_2 = A_4 \ln p_1 + B_4 \quad (5.8)$$

where p_2 and p_1 are the vapour pressures of the substances being compared at equal boiling points (or at equal reduced boiling points).

All four equations express a linear relationship between the corresponding quantities. The constants A and B can be determined graphically or analytically. The accuracy of the results of the calculation grows with an increasing similarity of the substances being compared.

The vapour pressures and boiling points can also be found by the rectification method, namely, the pressure is laid off along the axis of ordinates to a logarithmic scale and a straight line is plotted at an angle close to 45 degrees (from the bottom left-hand corner to the top right-hand one) which should express the vapour pressure of the substance (standard one) chosen for comparison. Next, according to the temperature dependence of the pressure for the standard substance, the temperature scale is marked off. In the coordinates obtained, the lines of $p=f(T)$ for other substances will be practically straight ones; for related compounds they converge at about the same point (if they are continued beyond the critical points). The latter circumstance permits us to assess the vapour pressure of a given homologue according to a single point if this relationship is known for the other members of the given homologous series.

Examples

1. The boiling points of methanol and water at $p=40$ mm Hg are respectively 5.0 and 34.1 °C, and at $p=100$ mm Hg they are 21.2 and 51.6 °C.

Using the boiling points of water at different pressures given below, find the boiling points of methanol at the same pressures. Employ Eq. (5.5) for the calculations.

Compare the results of the calculations with the experimental data given below:

p , mm Hg . . .	5	10	20	60	200	400	760
$t_{\text{H}_2\text{O}}^{\text{lg}}$, °C . . .	1.2	11.3	22.2	41.6	66.5	83.0	100.0
$t_{\text{CH}_3\text{OH}}^{\text{lg}}$, °C . . .	-25.3	-16.2	-6.0	12.1	34.8	49.9	64.7

Solution. We perform the calculations by the equation

$$T_{\text{CH}_3\text{OH}} = A_1 T_{\text{H}_2\text{O}} + B_1$$

whose constants we find on the basis of the boiling points of the liquids being compared at two pressures:

$$\text{for } p = 40 \text{ mm Hg: } \dots 5.0 + 273.2 = A_1 (34.1 + 273.2) + B_1$$

$$\text{for } p = 100 \text{ mm Hg: } \dots 21.2 + 273.2 = A_1 (51.6 + 273.2) + B_1$$

whence

$$A_1 = \frac{16.2}{17.5} = 0.9205$$

consequently

$$278.2 = 0.9205 \times 307.3 + B_1$$

$$\text{and } B_1 = 278.2 - 0.9205 \times 307.3 = -4.7$$

Hence

$$T_{\text{CH}_3\text{OH}} = 0.9205 T_{\text{H}_2\text{O}} - 4.7$$

Using the values of $T_{\text{H}_2\text{O}}$ given in the initial conditions of the example in this equation, we find $T_{\text{CH}_3\text{OH}}$. The results are given below:

p , mm Hg . . .	5	10	20	60	200	400	760
$t_{\text{CH}_3\text{OH}}$, °C . .	-25.3	-16.0	-6.0	11.9	34.8	50.0	65.6

The mean discrepancy between the found results and the values of $t_{\text{CH}_3\text{OH}}$ given in the initial conditions is about 0.2 K.

2. Show that Eq. (5.5) can be derived from Eq. (5.2) if it is assumed that at an equal vapour pressure the ratios of the heats of vaporization to the squares of the boiling points (in K) for the substances being compared are proportional to each other, i.e.

$$\frac{(\Delta H_{\text{vap}})_1}{T_1^2} = A_1 \frac{(\Delta H_{\text{vap}})_2}{T_2^2}$$

where A_1 is a proportionality factor.

Solution. Having written Eq. (5.2a) for two substances provided that $p_1 = p_2$, we get:

$$\frac{d \ln p}{dT_1} = \frac{(\Delta H_{\text{vap}})_1}{RT_1^2}$$

$$\frac{d \ln p}{dT_2} = \frac{(\Delta H_{\text{vap}})_2}{RT_2^2}$$

Division of the first equation by the second one yields

$$\frac{dT_2}{dT_1} = \frac{(\Delta H_{\text{vap}})_1/T_1^2}{(\Delta H_{\text{vap}})_2/T_2^2} = \text{const} = A_1$$

whence after integration we get Eq. (5.5).

3. The vapour pressures of *n*-propyl alcohol at $t=20$ and 70°C are respectively 14.5 and 239 mm Hg.

Plot a chart corresponding to Eq. (5.8) and find:

- (1) the vapour pressure of *n*-propyl alcohol at $t=40^\circ\text{C}$;
- (2) the boiling point at a pressure of 147 mm Hg.

Compare the results of the calculations with the experimentally found values respectively equal to 50.2 mm Hg and 60°C . Use water as the comparison substance. Take the data needed for the calculations from water property tables.

Solution. At 20 and 70°C the pressure of water vapour is respectively 0.023 83 and 0.3177 kgf/cm² or 17.5 and 233.7 mm Hg. We use

these two points to plot a chart of $\log p_{\text{C}_2\text{H}_5\text{OH}}$ versus $\log p_{\text{H}_2\text{O}}$ at $t_{\text{C}_2\text{H}_5\text{OH}} = t_{\text{H}_2\text{O}}$ (Fig. 24).

1. From water property tables we find that at $t = 40^\circ\text{C}$ the pressure of saturated water vapour (steam) is 0.0752 kgf/cm^2 (55.3 mm Hg).

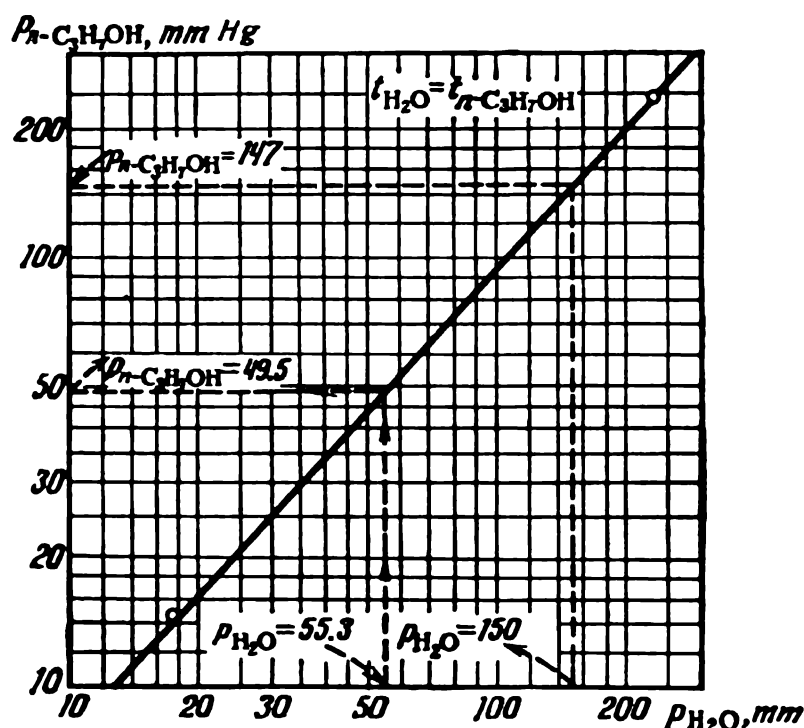


Fig. 24

From the chart we find $p_{\text{C}_2\text{H}_5\text{OH}} \approx 49.5 \text{ mm Hg}$ (the discrepancy is about 1.4%).

2. We find from Fig. 24 that $p_{\text{C}_2\text{H}_5\text{OH}} = 147 \text{ mm Hg}$ corresponds to $p_{\text{H}_2\text{O}} \approx 150 \text{ mm Hg} = 0.204 \text{ kgf/cm}^2$. Water will have such a vapour pressure at $t \approx 60.1^\circ\text{C}$. Consequently, $t_{\text{C}_2\text{H}_5\text{OH}} = 60.1^\circ\text{C}$ (the discrepancy is about 0.1 K).

Problems

1. Using the equation found in solving Example 1, calculate the boiling points of methyl alcohol at high pressures according to the boiling points of water given below. Compare the results with the experimental data:

$p, \text{ atm}$	2	5	10	20	30	40	50	60
$t_{\text{H}_2\text{O}}^{\text{lg}}, ^\circ\text{C}$	120.1	152.4	180.5	213.1	234.6	251.1	264.7	276.5
$t_{\text{CH}_3\text{OH}}^{\text{lg}}, ^\circ\text{C}$	84.0	112.5	138.0	167.8	186.5	203.5	214.0	224.0

2. The normal boiling point of benzaldehyde is 179.6°C , and its vapour pressure at 145°C is 300 mm Hg .

Construct a chart corresponding to Eq. (5.5) and find:

- (1) the boiling point at a pressure of 500 mm Hg ;
- (2) the vapour pressure at $t = 112.5^\circ\text{C}$.

Compare the results with the experimental data respectively equal to 163.7 °C and 112.5 mm Hg. Use water as the reference (comparison) substance. Take the data needed for the calculations from water property tables.

3. According to the data given in the initial conditions of Example 1 and Problem 1:

(1) derive Eq. (5.6);

(2) use this equation to calculate the boiling points of methyl alcohol at pressures of 5, 10, 20, 60, 200, 400 and 760 mm Hg and 2, 5, 10, 20, 30, 40, 50 and 60 atm.

Compare the results obtained with those calculated by Eq. (5.5).

4. Prove that Eq. (5.6) can be derived from Eq. (5.2) if it is assumed that at equal vapour pressures the ratios of the heats of vaporization to the absolute boiling point of the substances being compared are proportional to each other, i.e.

$$\frac{(\Delta H_{\text{vap}})_1}{T_1} = A_2 \frac{(\Delta H_{\text{vap}})_2}{T_2}$$

where A_2 is a proportionality factor.

5. What assumption must be made to derive Eq. (5.7) from Eq. (5.2)?

6. On the basis of the solutions of Example 2 and Problems 4 and 5, indicate the form which equations (5.5)-(5.7) will acquire if Eq. (5.4) holds for the liquids being compared.

7. Using the relationship

$$T_1 = \frac{(T_1)_{\text{n. b. p.}}}{(T_2)_{\text{n. b. p.}}} T_2$$

(see the result of solving Problem 6), find the boiling point of bromobenzene at $p=100$ mm Hg if at the same pressure the boiling point of iodobenzene is 119.1 °C and the normal boiling points of bromobenzene and iodobenzene are respectively 156.1 and 188.6 °C.

Compare the result with the experimentally found value equal to 90.6 °C.

8. Using the data given in the initial conditions of Example 1 and Problem 1:

(1) derive Eq. (5.7) for methanol;

(2) calculate its boiling points at pressures of 5, 10, 20, 60, 200, 400 and 760 mm Hg and 2, 5, 10, 20, 30, 40, 50 and 60 atm.

9. The coefficients A_1 , A_2 and A_3 of Eqs. (5.5)-(5.7) are determined by the following relationships:

$$\frac{(\Delta H_{\text{vap}})_1}{T_1^2} = A_1 \frac{(\Delta H_{\text{vap}})_2}{T_2^2} \quad (\text{a})$$

$$\frac{(\Delta H_{\text{vap}})_1}{T_1} = A_2 \frac{(\Delta H_{\text{vap}})_2}{T_2} \quad (\text{b})$$

$$(\Delta H_{\text{vap}})_1 = A_3 (\Delta H_{\text{vap}})_2 \quad (\text{c})$$

where T_1 and T_2 are the boiling points of the substances being compared

at the same pressure. For methanol and water we have $A_1=0.9205$, $A_2=1.016$, $A_3=1.121$ (see Example 1 and Problems 3 and 8).

Use these equations to find $(\Delta H_{\text{vap}})_{\text{CH}_3\text{OH}}$ at $p=1$ atm if at this pressure $(\Delta H_{\text{vap}})_{\text{H}_2\text{O}}=538.9$ cal/g.

Compare the result of the calculations with the experimentally found value of 262.8 cal/g.

Use the data given in the initial conditions of Example 1 and the results of solving Example 1 and Problems 3 and 8 for the calculations.

10. Find the heat of vaporization of methanol at $p=40$ atm with the aid of the data given in the initial conditions of Problem 9 if at this pressure the boiling point of water is 251.1°C and the heat of vaporization of water is 408.4 kcal/kg. The boiling point of methanol is 203.5°C .

Compare the result of the calculations with the experimentally found value (141.3 cal/g).

11. The saturated vapour pressures for water and methanol at 5°C are respectively 6.5 and 40 mm Hg, and at 50°C the relevant values are 92.5 and about 400 mm Hg.

Use the vapour pressures of water given below to find the vapour pressures of methanol at the same temperatures. Compare the results obtained with the values of the methanol given below:

$t, ^\circ\text{C}$	0	30	70
$p_{\text{H}_2\text{O}}, \text{ mm Hg}$	4.575	31.82	233.7
$p_{\text{CH}_3\text{OH}}, \text{ mm Hg}$	~ 25	145	927

12. The heats of vaporization of ethylidene chloride and silicon chloride at $t\approx 56.6^\circ\text{C}$ are approximately 68.7 and 39.7 cal/g, respectively, and the vapour pressure over both liquids is 741 mm Hg.

Find the vapour pressure of silicon chloride at 20.4°C if the vapour pressure of ethylidene chloride at this temperature is 200 mm Hg.

13. Prove that Eq. (5.8) can be obtained from Eq. (5.2) both when $T_1=T_2$ and when $T_1/(T_1)_{\text{cr}}=T_2/(T_2)_{\text{cr}}$.

14. The vapour pressure of α -pinene ($\text{C}_{10}\text{H}_{16}$) at 90.5 and 110.3°C is 100 and 200 mm Hg, respectively.

Find $t_{\text{n.b.p.}}$ and $p_{t=72}$ by the method of rectification. Plot the chart according to the relationship $p=f(t)$ for water. Compare the result with the experimentally found values equal respectively to 156°C and 49 mm Hg.

5.3. CRITICAL PARAMETERS

The coordinates of the critical point are determined by the simultaneous solution of an equation of state and the equations

$$\left(\frac{\partial p}{\partial V}\right)_{T_{\text{cr}}} = 0 \quad (5.9)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T_{\text{cr}}} = 0 \quad (5.9a)$$

expressing the conditions of inflection of the critical isotherm.

The values of p_{cr} and T_{cr} can be found experimentally. Besides, one quantity can be calculated analytically or graphically from the other one using the relationship between the boiling point and the pressure of the saturated vapour.

The value of V_{cr} is usually determined by means of the *rule of the straight diameter*, according to which the half-sum of the densities of a boiling liquid (ρ^{lq}) and its saturated vapour (ρ^g) is a linear function of the temperature:

$$\frac{\rho^{lq} + \rho^g}{2} = a + bt \quad (5.10)$$

A number of semi-empirical and empirical equations were also proposed. Thus, it is possible to use the equation

$$\frac{T_{eq}}{T_{cr}} = 0.283 \left(\frac{M}{\rho_{n.b.p.}^{lq}} \right)^{0.18} \quad (5.11)$$

where M = molecular weight

$\rho_{n.b.p.}^{lq}$ = density of the liquid at the normal boiling point, g/cm³

T_{eq} = temperature at which the liquid is in equilibrium with the saturated vapour, 22.4 dm³ containing one mole of vapour.

The value of T_{eq} can be found from Fig. 25, which contains a plot of $T_{eq} - T_{n.b.p.}$ versus $T_{n.b.p.}$ (the *Kireev-Watson method*).

Meissner and Redding proposed the equations

$$V_{cr} = (0.377P + 11.0)^{1.25} \quad (5.12)$$

$$T_{cr} = 1.70T_{n.b.p.} - 2 \quad (5.13)$$

$$T_{cr} = 1.41T_{n.b.p.} + 66 - 11F \quad (5.14)$$

$$T_{cr} = 1.41T_{n.b.p.} + 66 - r(0.383T_{n.b.p.} - 93) \quad (5.15)$$

$$T_{cr} = 1.027T_{n.b.p.} + 159 \quad (5.16)$$

$$p_{cr} = \frac{20.8T_{cr}}{V_{cr} - 8} \quad (5.17)$$

where P = parachor ($P = \frac{M\sigma^{\frac{1}{4}}}{\rho^{lq} - \rho^g}$, in which σ is the surface tension)

F = number of fluorine atoms in a molecule of the substance

r = ratio between the number of acyclic atoms of carbon and their total number in a molecule.

Equation (5.13) is used for elements or simple substances regardless of their boiling point (if $T_{n.b.p.}$ exceeds 235 K); Eq. (5.14) for substances containing halogens and sulphur; Eq. (5.15) for aromatic

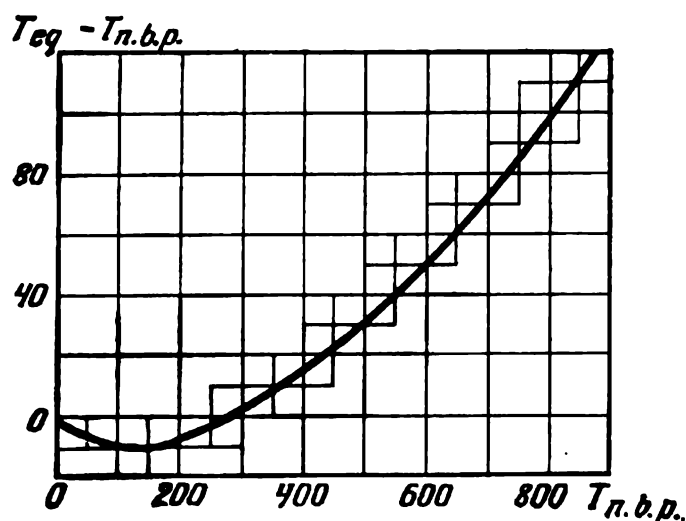


Fig. 25

compounds and naphthenes containing no halogens and sulphur, and Eq. (5.16) for other substances containing no halogens and sulphur. The last three equations may be used for compounds having a normal boiling point from 236 to 600 K.

The following relationship can be used for an approximate assessment of the critical parameters

$$\frac{p_{cr}V_{cr}}{T_{cr}} \approx 22 \quad (5.18)$$

and also the corollaries of the principle of corresponding states (Chapter Six).

Examples

1. Show using Eq. (5.9) and the equation

$$C_p = C_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p$$

(see Problem 6 in Sec. 3.1) that at the critical point we have $C_{p_{cr}} = \infty$.

Solution. In accordance with the relationship

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

and Eq. (5.9) we have

$$-\left(\frac{\partial p}{\partial V} \right)_T = \frac{(\partial p / \partial T)_v}{(\partial V / \partial T)_p} = 0$$

Since the derivative $(\partial p / \partial T)_v$ is a finite quantity at the critical point, then $(\partial V / \partial T)_p = \infty$. Hence in accordance with the equation given in the initial conditions of the example, we have $C_{p_{cr}} = \infty$.

2. The density of boiling helium and its saturated vapour has the following values:

T , K	4.59	4.23	3.90	3.30	2.56
ρ^{lq} , g/cm ³ . . .	0.1165	0.1253	0.1311	0.1395	0.1457
ρ^g , g/cm ³ . . .	0.023 68	0.016 37	0.011 76	0.006 435	0.002 079
T , K			2.37	2.30	
ρ^{lq} , g/cm ³			0.1466	0.1469	
ρ^g , g/cm ³			0.001 368	0.001 159	

1. Find the critical density of helium with the aid of the rule of the straight diameter if $T_{cr} = 5.19$ K. Perform the calculations graphically.

2. What is the density of boiling helium at 4.71 K if $\rho^g = 0.026 99$ g/cm³? Compare the result of the calculations with the value of $\rho^{lq} = 0.1139$ g/cm³.

3. Find the temperature at which superheated helium vapour will begin to condense if $\rho^g = 0.120 \text{ g/cm}^3$.

Solution. We plot a chart (Fig. 26) in the coordinates ρ^{lq} and ρ^g versus T . After finding at each temperature the value of $(\rho^{lq} + \rho^g)/2$, we connect the points obtained and continue the line to its intersection with the perpendicular erected from the point T_{cr} .

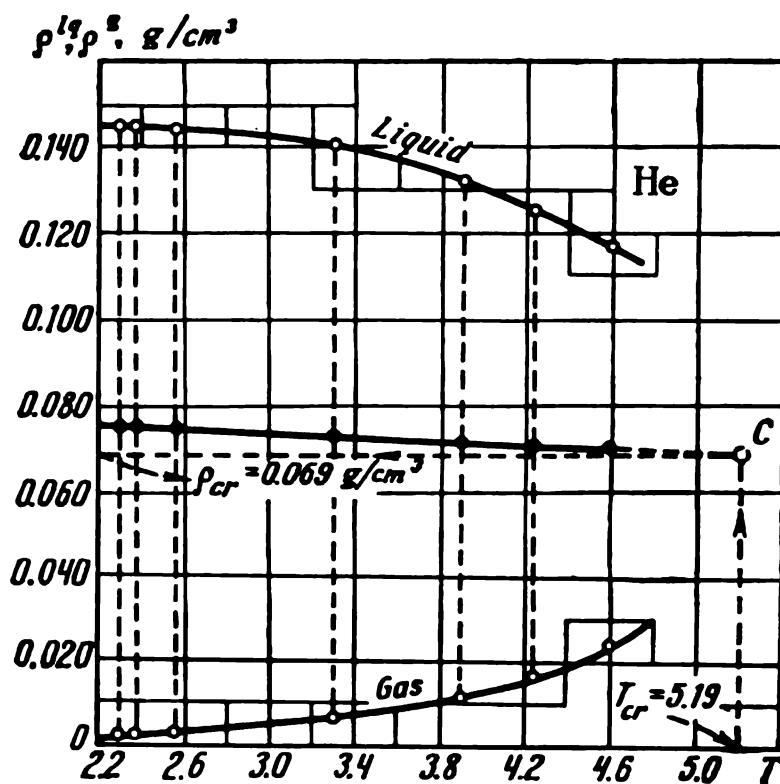


Fig. 26

1. The point of intersection C corresponds to $\rho_{cr}^{lq} = 0.069 \text{ g/cm}^3$ or $V_{cr} \approx \frac{4.00}{0.069} = 57.97 \text{ cm}^3$.

2. Since at $T = 4.71 \text{ K}$ we have $(\rho^{lq} + \rho^g)/2 \approx 0.0695$, then $(\rho^{lq} + 0.02699)/2 = 0.0695$ and $\rho^{lq} \approx 0.112 \text{ g/cm}^3$, which differs from the experimentally found value by 1.7%.

3. We find from the chart that $T \approx 4.44 \text{ K}$.

Problems

1. Show that if Eq. (4.1) holds, the critical parameters of a substance are

$$p_{cr} = \frac{a}{27b^2}; \quad T_{cr} = \frac{8a}{27Rb} \quad \text{and} \quad V_{cr} = 3b$$

Using these relations, determine the constants a and b of Eq. (4.1) for methyl cyanide (CH_3CN) if $t_{cr} = 274.7^\circ\text{C}$ and $p_{cr} = 47.7 \text{ atm}$.

2. Find expressions for calculating p_{cr} , V_{cr} and T_{cr} if the Dietze equation

$$p(V-b) = RT \exp(a/RTV)$$

can be applied.

3. What does the quantity $(\partial V/\partial p)_T$ equal at the critical point (take a gas described by the van der Waals equation as an example)?

4. Find the equation of the straight diameter for oxygen if $t_{cr} = -118.8^\circ\text{C}$, $V_{cr} = 0.00233\text{ m}^3/\text{kg}$ and at $t = -182^\circ\text{C}$ we have $\rho^{lq} = 1.1415$ and $\rho^g = 0.0051\text{ g/cm}^3$.

5. Use Eq. (5.4) and the approximate relationship $T_{cr} = \frac{3}{2}T_{n.b.p.}$ to find t_{cr} for acetone if $(\Delta H_{vap})_{n.b.p.} = 123.7\text{ cal/g}$.

Compare the result with the most authentic value given in Appendix 8.

6. The following three equations were proposed to express the temperature dependence of the saturated vapour pressure of ethane in the region of high pressures:

$$\log p = -\frac{810.16}{T} + 4.3371$$

$$\log p = 4.6728 - \frac{1030.63}{312.23 + t}$$

$$\log p = -\frac{780.24}{T} + 4.2563 - 0.000103T + 1.4 \times 10^{-11}(T - 238)^5$$

Determine the critical pressure of ethane if $t_{cr} = 32.3^\circ\text{C}$ for it.

Use the results of the calculations to indicate which of the equations given above is the most accurate for calculating the pressure of vapour in the direct proximity to the critical point, if the critical pressure of ethane according to the most authentic data is 48.2 atm.

7. At high temperatures, the saturated vapour pressure of butene-1 has the following values:

$t, ^\circ\text{C}$	110	120	130	140
p, atm	21.31	25.51	30.29	35.69

Find the critical temperature if $p_{cr} = 40.0\text{ atm}$. Use the graphical method and compare the result with the most authentic value equal to 147.2°C . The recommended scales are 0.0001 K^{-1} in 50 mm for $1/T$ and 0.1 in 50 mm for $\log p$.

8. The normal boiling point of ethane is -88.62°C , and the density of the liquid boiling at this temperature is 0.546 g/cm^3 . Use the Kireev-Watson method to calculate the critical temperature and compare it with the experimentally established value equal to 32.2°C .

9. Find the critical parameters of ethyl isobutyrate ($\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$) if $t_{n.b.p.} = 110^\circ\text{C}$. Compare the results with the experimental data, namely, $t_{cr} = 280^\circ\text{C}$, $p_{cr} = 30\text{ atm}$ and $\rho_{cr} = 0.276\text{ g/cm}^3$.

Use the following values of the parachors for the calculations: 4.8 (C), 17.1 (H) and 20 (O).

10. Using the values of t_{cr} and p_{cr} indicated in the initial conditions of the preceding problem, calculate the critical density of ethyl isobutyrate. Use Eq. (5.18) for the calculations.

Compare the result of the calculations with the value of $\rho=0.276 \text{ g/cm}^3$.

5.4. HEAT CAPACITIES OF COEXISTING PHASES AND HEATS OF PHASE TRANSITIONS

The heat capacity of an equilibrium (saturated) phase is

$$C_{\text{eq}} = C_p - T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_{\text{eq}} \quad (5.19)$$

where $(\partial p/\partial T)_{\text{eq}}$ is taken along the equilibrium curve.

For a boiling liquid at temperatures far from the critical one and for a melting crystalline body, the derivative $(\partial V/\partial T)_p$ is very small; consequently, the second term in the right-hand part of Eq (5.19) may be neglected for them.

The exact temperature dependence of the heat of phase transition is expressed by Eq. (5.1). In addition, it is possible to use the strict thermodynamic relationship

$$\frac{\partial \Delta H}{\partial T} = \Delta C_{\text{eq}} + \frac{\Delta H}{T} \quad (5.20)$$

which in accordance with Eqs. (5.19) and (5.1) can be transformed to

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \frac{\Delta H}{T} \left[1 - \frac{T}{\Delta V} \left(\frac{\partial \Delta V}{\partial T} \right)_p \right] \quad (5.21)$$

In these equations the quantities ΔC_{eq} , ΔH , ΔC_p and ΔV are the differences between the corresponding molar characteristics of the coexisting phases.

Equations (5.20) and (5.21) mainly serve for checking the reliability of the values of thermodynamic quantities. Equation (5.20) is also used for calculating the heat capacity of saturated vapour.

Since the derivative $(\partial \Delta V/\partial T)_p$ is not great for melting and transition from one modification to another, for these equilibria Eq. (5.21) becomes

$$\frac{\partial \Delta H}{\partial T} \approx \Delta C_p + \frac{\Delta H}{T} \quad (5.22)$$

For vaporization—the most important phase transition in practice—the quantity ΔV may be assumed equal to V^g at $T \ll T_{\text{cr}}$. Hence, considering saturated vapour to be an ideal gas, from Eq. (5.21) we get

$$\frac{\partial \Delta H}{\partial T} \approx C_p^g - C_p^{\text{lg}} \quad (5.23)$$

[This equation is less accurate than Eq. (5.20) when C_p^{lg} is substituted for $C_{\text{eq}}^{\text{lg}}$ in it.]

The temperature dependence of ΔH_{vap} can also be found with the aid of various semi-empirical and empirical methods, in particular by means of the *Kudryavtsev equations*

$$\frac{\Delta H_{\text{vap}}}{T} \approx A_1 \ln T + B_1 \quad (5.24)$$

$$\frac{\Delta H_{\text{vap}}}{T} \approx A_2 \ln T + B_2 T + C \quad (5.25)$$

and by means of the following equation recommended by the author:

$$\frac{(\Delta H_{\text{vap}})_2}{(\Delta H_{\text{vap}})_1} \approx K \quad (5.26)$$

where A_1 , B_1 , A_2 , B_2 , C and K = constants

$(\Delta H_{\text{vap}})_1$ and $(\Delta H_{\text{vap}})_2$ = heats of vaporization of the substances being compared at temperatures at the same distance from their critical temperatures.

Other methods of calculating ΔH are considered in Secs. 5.1, 5.2, 6.2 and also in Chapter Seven (p. 160).

Examples

1. Find C_{eq}^g for steam at 100 °C with the aid of Eq. (5.19). Assume that $V^g = 1.673$, $V^{lq} = 0.001\,043\,5$ m³/kg and $\Delta H_{\text{vap}} = 538.9$ kcal/kg. Compare the result with the experimentally found value of $C_{\text{eq}}^g = -1.07$ cal/g·K.

Assume that $p = 1$ kgf/cm² and take into account that at 100 and 110 °C v respectively equals 1.730 and 1.781 m³/kg, and H respectively equals 639.1 and 644.2 kcal/kg.

Solution. In accordance with Eq. (5.1) we have

$$\frac{\partial p}{\partial T} = \frac{538.9 \times 41.293}{373.2 \times (1.673 - 1.0435)} = 0.035\,66$$

Let us consider that

$$\left(\frac{\partial V}{\partial T}\right)_p \approx \left(\frac{\Delta V}{\Delta T}\right)_p \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \approx \left(\frac{\Delta H}{\Delta T}\right)_p$$

where ΔV , ΔH and ΔT are small changes in the volume and enthalpy of the steam and the corresponding insignificant change in the temperature along the isobar.

Consequently,

$$\left(\frac{\partial V}{\partial T}\right)_p \approx \frac{1.781 - 1.730}{110 - 100} = 0.0051 \text{ m}^3/\text{kg} \cdot \text{K} = 5.1 \text{ cm}^3/\text{g} \cdot \text{K}$$

and

$$C_p \approx \frac{644.2 - 639.1}{110 - 100} = 0.51 \text{ kcal/kg} \cdot \text{K} = 0.51 \text{ cal/g} \cdot \text{K}$$

Using the found values in Eq. (5.19), we get

$$C_{eq}^g = 0.51 - \frac{373.2 \times 5.1 \times 0.03566}{41.293} = -1.13 \text{ cal/g} \cdot \text{K}$$

which differs from the value indicated in the initial conditions by 5.3%.

2. In studying the thermodynamic properties of benzene, it was established that $(C_{sat})_{C_6H_6}^g$ is positive within the temperature range from 72 to 267 °C, and is negative at temperatures below 72 and above 267 °C. Can these data be used to judge the nature of the orthobaric curve on a T - S diagram for benzene? What conclusions can be made on the basis of the results obtained if the values of $(C_{eq})^g$ for benzene and water vapours are compared?

Solution. From the relationship

$$C_{eq} = \left(\frac{\partial Q}{\partial T} \right)_{eq} = T \left(\frac{\partial S}{\partial T} \right)_{eq}$$

obtained from Eq. (3.1) it follows that for benzene vapours at $t=72$ to 267 °C we have $(\partial S/\partial T)_{eq} > 0$ and at $72 > t > 267$ °C we have $(\partial S/\partial T)_{eq} < 0$.

For water vapour (steam) at all temperatures we have $(\partial S/\partial T)_{eq} < 0$ (see Fig. 21).

For the liquid phase, regardless of the nature of the substance,

$$C_{eq}^{lq} \approx C_p^{lq} > 0$$

Therefore the branch of the orthobaric curve relating to the boiling liquid will be characterized by the inequality

$$\left(\frac{\partial S}{\partial T} \right)_{eq} > 0$$

The results obtained in solving this example are shown schematically in Fig. 27, which also depicts curves of adiabatic compression (OB) and adiabatic expansion (OA) of the saturated vapour. Inspection of this figure shows that if adiabatic compression of benzene vapour (within the range from 72 to 267 °C) results in its moistening, then the adiabatic compression of water vapour (steam) results in its being superheated.

The condensation of saturated water vapour upon adiabatic expansion is one of the reasons why the barometric pressure drops in rainy weather.

3. Show that Eq. (5.21) can be transformed to

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \left(\frac{\partial \Delta H}{\partial p} \right)_T \frac{\partial p}{\partial T}$$

Solution. If Eq. (5.21) is rewritten in the form

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \frac{\Delta H}{T} - \frac{\Delta H}{\Delta V} \left(\frac{\partial \Delta V}{\partial T} \right)_p$$

then by Eq. (5.1)

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p + \Delta V \frac{\partial p}{\partial T} - T \frac{\partial p}{\partial T} \left(\frac{\partial \Delta V}{\partial T} \right)_p = \Delta C_p + \left[\Delta V - T \left(\frac{\partial \Delta V}{\partial T} \right)_p \right] \frac{\partial p}{\partial T}$$

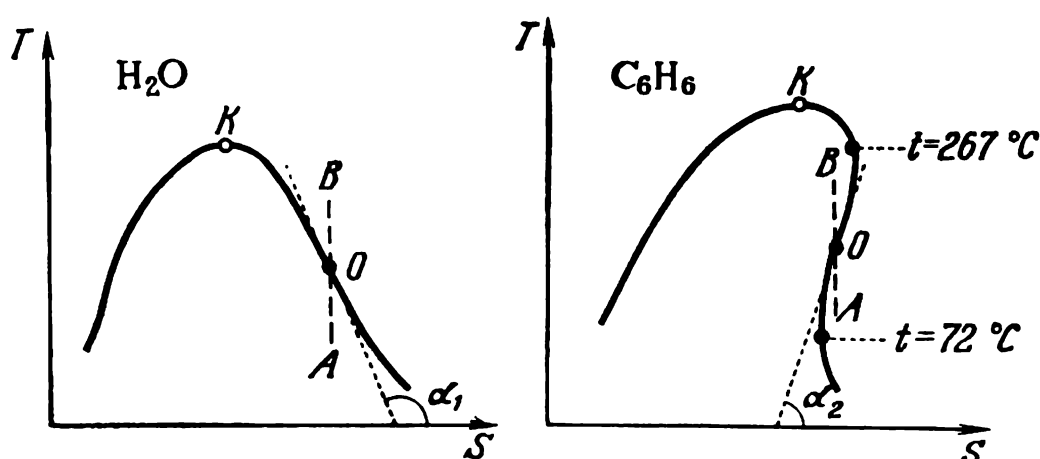


Fig. 27

Since for each of the equilibrium phases we have

$$\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p$$

then introducing $(\partial \Delta H / \partial p)_T$ instead of the expression in brackets, we get the sought equation.

4. The heat of vaporization of benzene at $t=40$ and 120 °C is respectively 421.4 and 362.8 J/g.

Find the molar heat of vaporization of benzene at $t=0, 80, 160, 200, 240$ and 280 °C.

Compare the results with the reference values given below:

$t, ^\circ\text{C}$	0	80	160	200	240	280
$\Delta H_{\text{vap}}, \text{ cal/mol}$	8360	7359	6133	5351	4227	2141

Solution. Converting the data given in the initial conditions of the example to cal/mol, we get

$$\Delta H_{t=40} = 421.4 \times 78.1 \times 0.239 = 7866 \text{ cal/mol}$$

$$\Delta H_{t=120} = 362.8 \times 78.1 \times 0.239 = 6772 \text{ cal/mol}$$

Next we plot the following two points on a chart of $\Delta H_{\text{vap}}/T$ versus $\log T$ (Fig. 28):

$$\text{point 1} - \log T_1 = 2.4958 \quad \text{and} \quad \frac{\Delta H_{\text{vap}}}{T} = \frac{7866}{313.2} = 25.11;$$

$$\text{point 2} - \log T_2 = 2.5946 \quad \text{and} \quad \frac{\Delta H_{\text{vap}}}{T} = \frac{6772}{393.2} = 17.22$$

Connecting these points by a straight line and continuing it in both

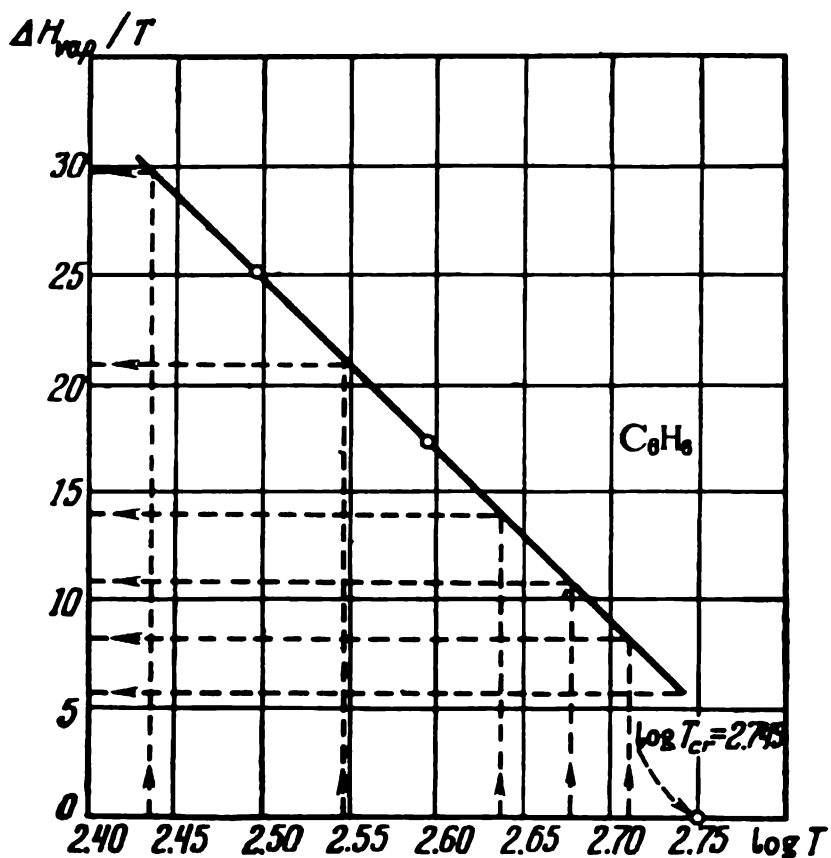


Fig. 28

directions, in accordance with Eq. (5.24), by extrapolation and interpolation of the value of ΔH_{vap} at the given values of t , we find:

t	0	80	160	200	240	280
$\log T$	2.436	2.548	2.637	2.675	2.710	2.743
$\Delta H_{\text{vap}}/T$	29.8	20.9	14.0	11.0	8.2	5.6
ΔH_{vap}	8130	7380	6070	5210	4210	3100

If we exclude the last value, the discrepancy between the experimentally found and the calculated data will be about 1.4%.

5. The heat of vaporization of carbon tetrachloride at $t=80^\circ\text{C}$ is 7024 cal/mol.

Find ΔH_{vap} at 260°C by Eq. (5.26) and compare it with the experimentally found value of this quantity (3063 cal/mol) if t_{cr} for carbon tetrachloride is 283.1°C . Take water as the standard substance.

Use water property tables for the calculations.

Solution. The heat of vaporization of CCl_4 is given at

$$(t_{\text{cr}} - t)_{\text{CCl}_4} = (t_{\text{cr}} - t)_{\text{H}_2\text{O}} = 283.1 - 80 = 203.1^\circ\text{C}$$

therefore

$$t_{\text{H}_2\text{O}} = 374.2 - 203.1 = 171.1^\circ\text{C}$$

According to water property tables for this temperature we find

$$(\Delta H_{\text{vap}})_{\text{H}_2\text{O}} \approx 488.3 \text{ kcal/kg (8799 cal/mol)}$$

Hence, for CCl_4 the constant of Eq. (5.26) is

$$K = \frac{7024}{8799} = 0.798$$

We determine ΔH_{vap} for CCl_4 at $t = 260^\circ\text{C}$:

$$(t_{\text{cr}} - t)_{\text{CCl}_4} = 283.1 - 260 = 23.1 \text{ K}$$

therefore

$$t_{\text{H}_2\text{O}} = 374.2 - 23.1 = 351.1^\circ\text{C}$$

According to water property tables for this temperature we find

$$(\Delta H_{\text{vap}})_{\text{H}_2\text{O}} = 208.9 \text{ kcal/kg (3764 cal/mol)}$$

Using the found value of K_{CCl_4} , we get

$$(\Delta H_{\text{vap}})_{\text{CCl}_4} = 3764 \times 0.798 = 3004 \text{ cal/mol,}$$

which differs from the value given in the initial conditions by 2.0%.

Problems

1. Use Eq. (5.20) to calculate C_{eq} for water at $t = 100^\circ\text{C}$ and compare the result obtained with the ones found by calculations according to Eq. (5.19) (see Example 1).

Use the following data for the calculations:

$t, ^\circ\text{C}$	99	100	101
$\Delta H_{\text{vap}}, \text{ kcal/kg}$	539.5	538.9	538.3

2. Figure 29 shows the temperature dependence of ΔH_{vap} for Freon-21 (CHCl_2F).

Find $C_{\text{eq}}^g - C_{\text{eq}}^{\text{liq}}$ at $t = 0, 60$ and 130°C .

3. Show that with certain assumptions the exact equation (5.19) may be replaced for a saturated vapour with the relationship

$$C_{\text{eq}}^g = C_p^g - \frac{\Delta H_{\text{vap}}}{T}$$

Find the heat capacity of saturated steam at 100°C with the aid of this equation. Take the data needed from the solution of Example 1. Compare the result with what was obtained in solving Example 1 and Problem 1.

4. The heat capacity of solid and liquid *m*-xylene at $T_{n.m.p.}=225$ K is respectively equal to approximately 29.22 and 39.71 cal/mol·K. The heat of fusion is about 2800 cal/mol.

Find the approximate value of the change in the heat of fusion with the temperature related to one kelvin.

5. The heat of vaporization of *n*-pentane at $t=33.5$ °C is 84.14 cal/g. The heat capacity of liquid pentane at $t=34$ °C is approximately 0.524 cal/g, and that of gaseous pentane is approximately 0.40 cal/g.

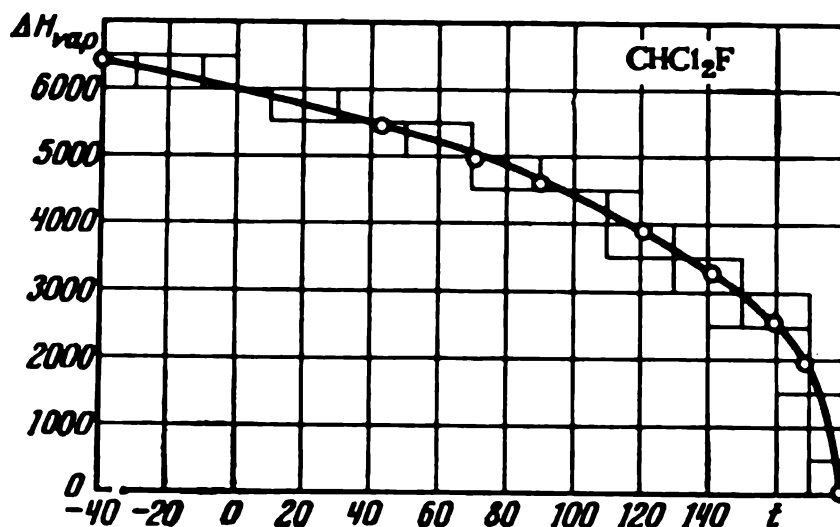


Fig. 29

Find the heat of vaporization at 6.4 °C and compare it with the experimentally found value of 91.87 cal/g.

6. The heats of vaporization of ethane at $T=200$ and 270 K are respectively equal to 3226 and 2290 cal/mol.

Derive Eq. (5.24).

Use it to calculate ΔH_{vap} at $T=240$ and $T=295$ K.

Compare the results of the calculations with the values found from experimental data and equal respectively to 2830 and approximately 1381 cal/mol.

Explain the reasons for the discrepancy of the results.

7. The heats of vaporization of ethane at 200, 240 and 270 K are respectively 3226, 2830 and 2290 cal/mol.

Derive Eq. (5.25).

Find ΔH_{vap} at 280 K.

Compare the result with the value of $\Delta H_{vap}=2014$ cal/mol found from experimental data.

8. The heat of vaporization of propane at $t_{n.b.p.}=-42.0$ °C is 4490 cal/mol; the heat of vaporization of heptane at $t_{n.b.p.}=98.3$ °C is 7660 cal/mol.

Assuming that for the homologous series ethane-octane the constant of Eq. (5.26) changes linearly with a change in the number of carbon atoms, find:

- (1) the dependence of the constant K of Eq. (5.26) on the number of carbon atoms;
- (2) the heat of vaporization of ethane at 184.1 K;
- (3) ΔH_{vap} of butane at $t_1 = -0.5$ and $t_2 = 94.45$ °C.

Compare the results with the values found according to experimental data (respectively 3514, 5350 and 63.20 cal/g). Take the heats of vaporization of water needed for calculation from water property tables.

Chapter Six

GENERALIZED METHODS OF CALCULATION *

6.1. GASES

The generalized methods of calculating the thermodynamic quantities came into the greatest favour for calculating the properties of gases. These methods are based on the principle of corresponding states and permit different properties of substances to be approximately calculated within a considerable range of temperatures and pressures with the aid of equations or charts according to the reduced temperature $\tau = T/T_{cr}$ and the reduced pressure $\pi = p/p_{cr}$ (using in some cases the known values of certain properties).

The *pressure-volume-temperature* relationship is determined according to the dependence of the compression factor Z on π and τ (Fig. 30).

The compression factor of a mixture Z_{mix} can be found in the following ways:

(1) Fig. 30 is used to determine the compression factor Z_i of each component, and then Z_{mix} is calculated by the equation

$$Z_{mix} = \sum x_i Z_i \quad (6.1)$$

(2) the mixture is considered as a pure gas and the values of the pseudocritical parameters

$$T'_{cr} = \sum x_i (T_{cr})_i \quad \text{and} \quad p'_{cr} = \sum x_i (p_{cr})_i \quad (6.2)$$

are ascribed to it. Next the pseudoreduced parameters

$$\tau' = T/T'_{cr} \quad \text{and} \quad \pi' = p/p'_{cr}$$

are calculated and, finally, the value of Z_{mix} is determined from Fig. 30.

After finding the value of Z_{mix} in one of the ways described above, the volume of the mixture is computed by Eq. (4.5). If p and V or T and V are given for the calculations instead of p and T , then the trial and error method is used.

The *fugacity* is calculated with the aid of a plot of the activity coefficient γ versus π and τ . Such a plot is shown in Fig. 31; more accurate

* For the values of the critical temperature and critical pressure needed for calculations see Appendix 8.

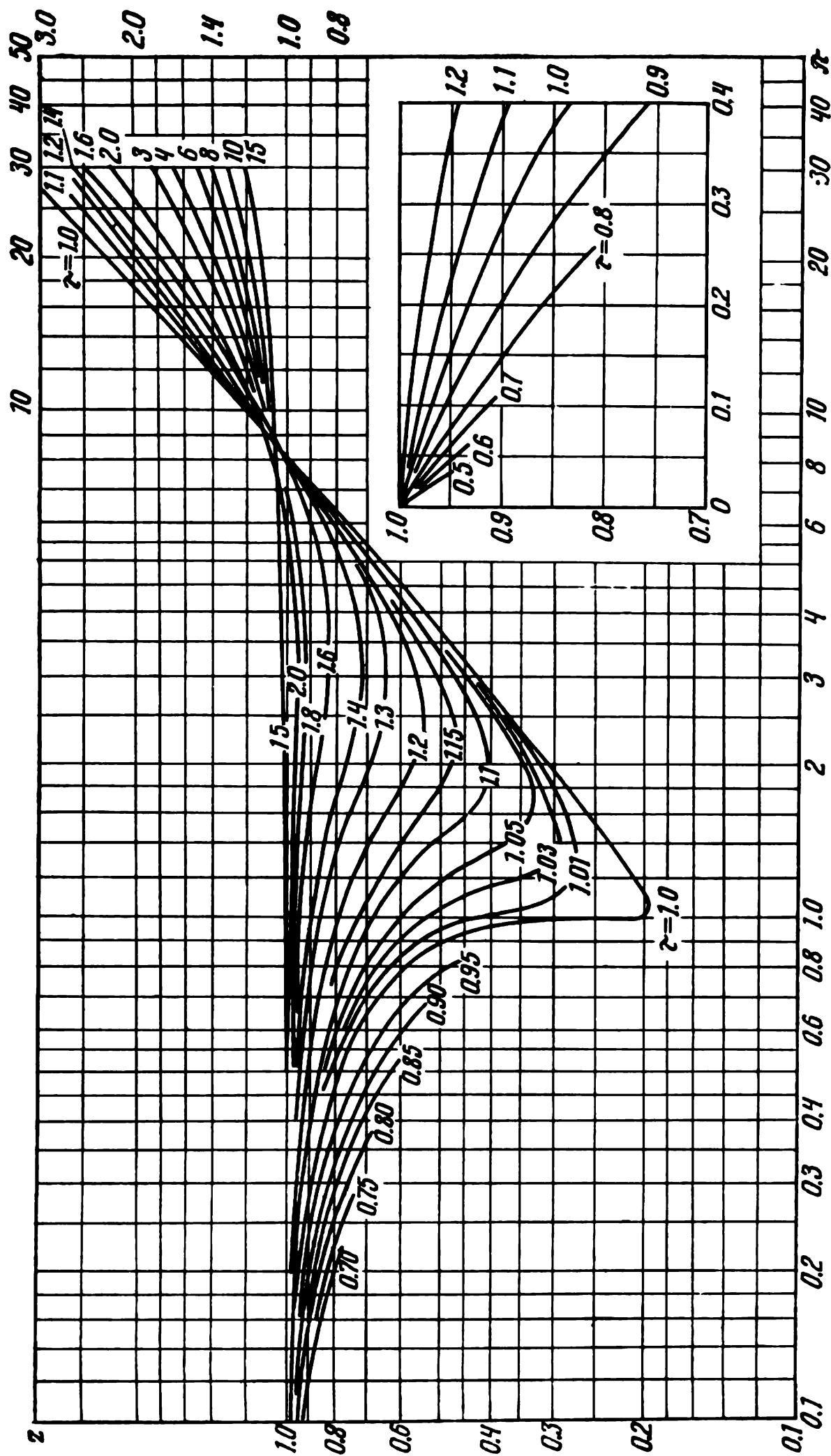


Fig. 30

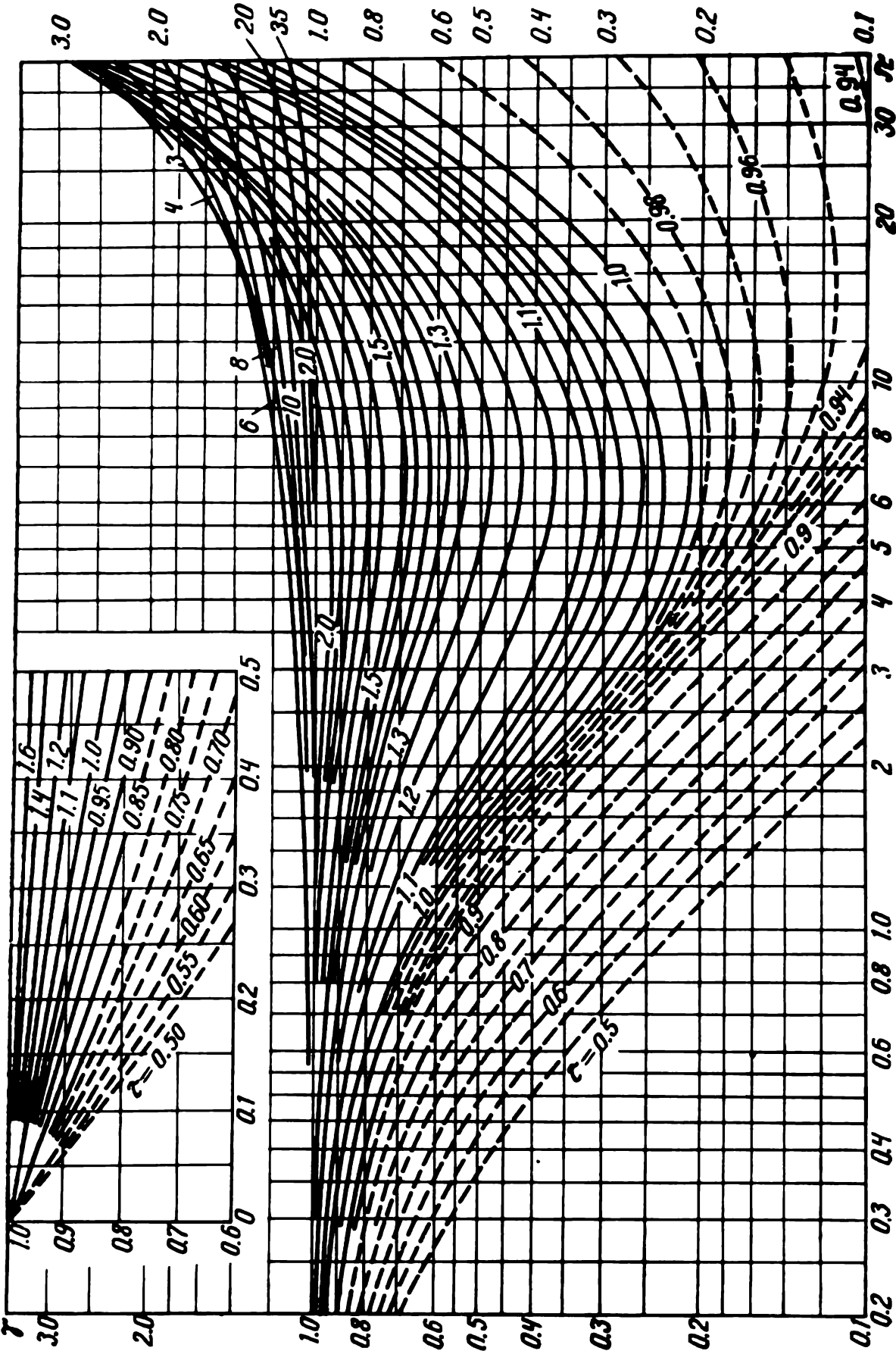


Fig. 31

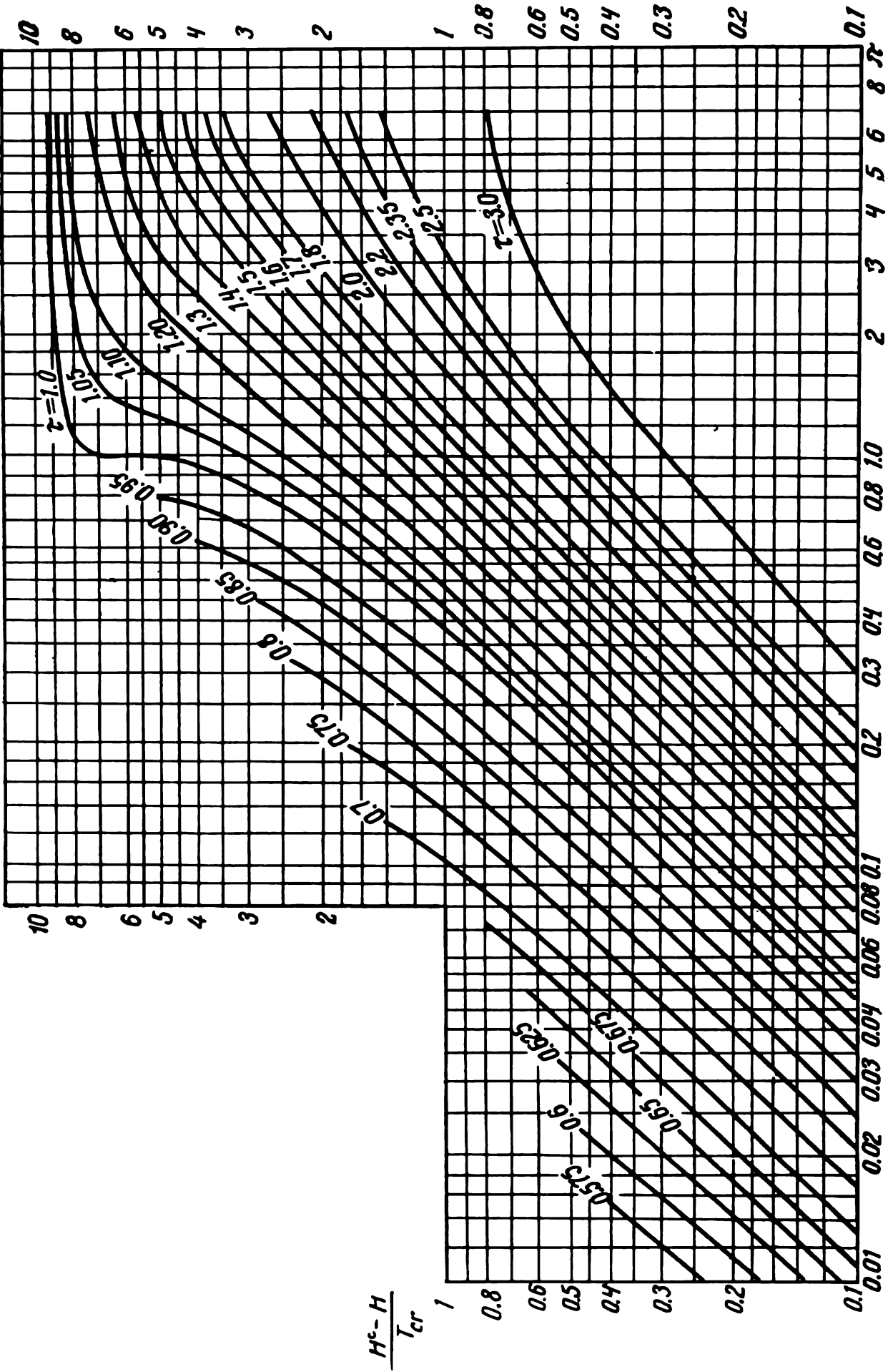


Fig. 32

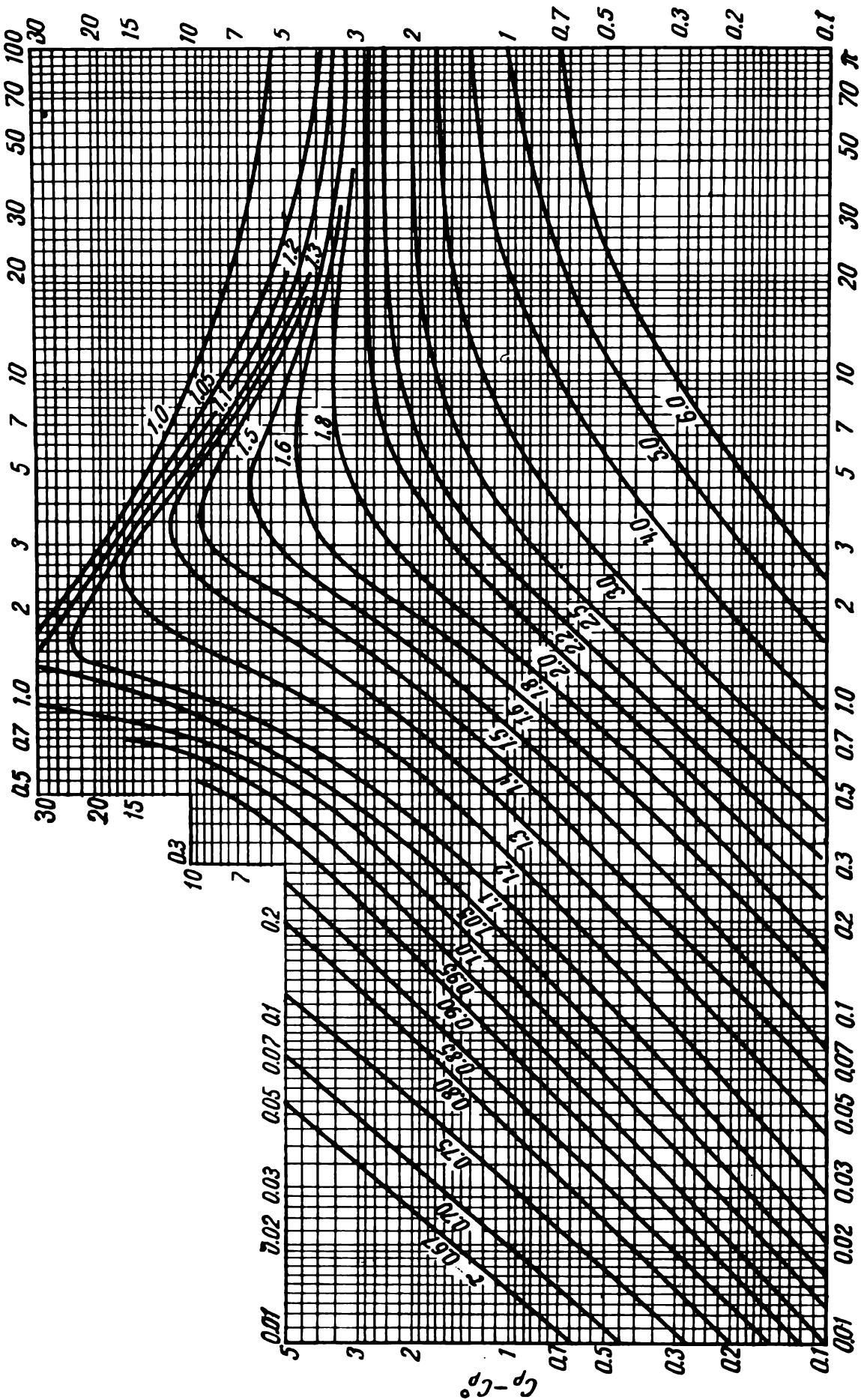


Fig. 33

values of γ can be found from the table in Appendix 9, which covers a greater range of values of π and τ than the plot.

The temperature and pressure dependences of the *enthalpy* and *heat capacity* are calculated with the aid of plots of $(H^\circ - H)/T_{cr}$ versus π and τ (Fig. 32) and $C_p - C_p^\circ$ versus π and τ (Fig. 33). Here H°

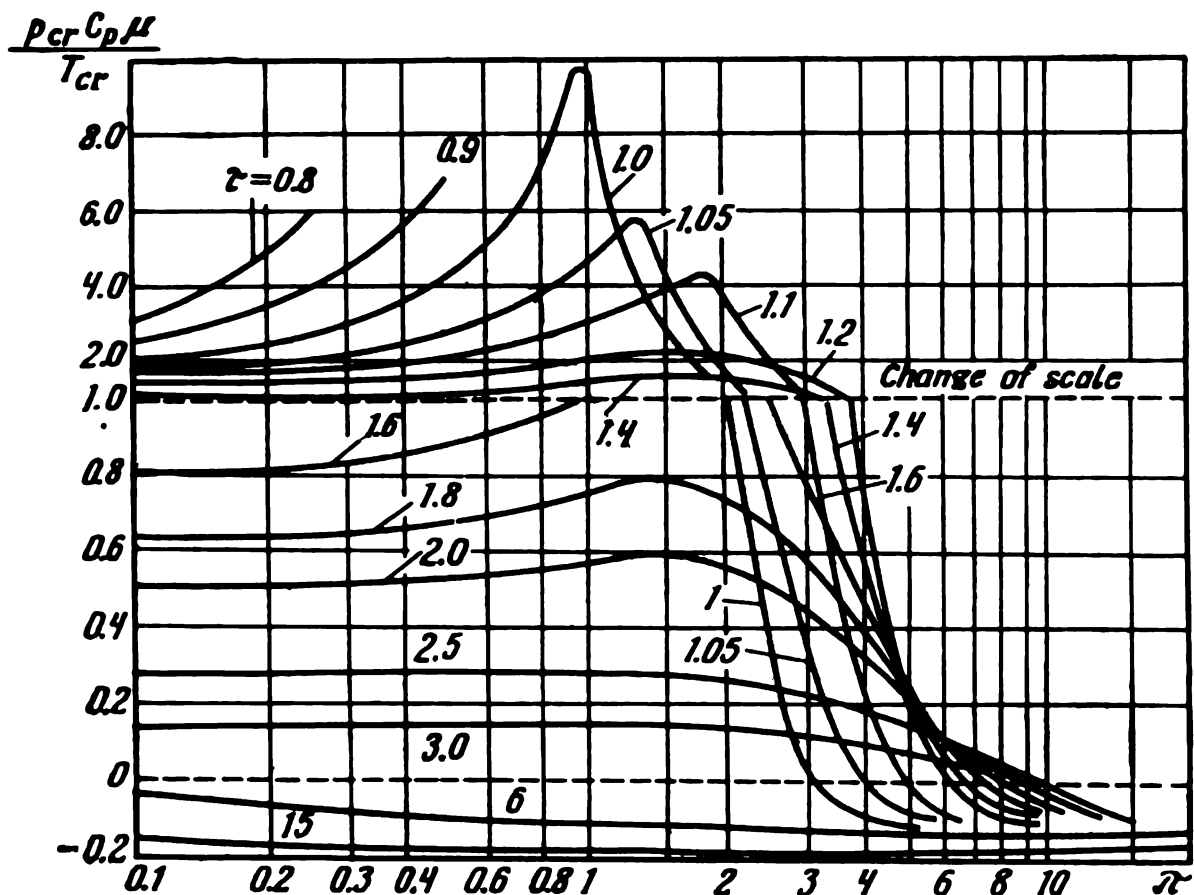


Fig. 34

and C_p° are the enthalpy and heat capacity at the given temperature and an infinitely low (practically atmospheric) pressure.

The *Joule-Thomson coefficient* can be calculated with the aid of Fig. 34 and the equation

$$\Delta T = \frac{RT_1^2 \ln(\gamma_1''/\gamma_1')}{(C_p^\circ)_{av} T_{cr}(\tau_1'' - \tau_1')} \quad (6.3)$$

where γ_1' and γ_1'' are taken at p_1 and respectively τ_1' and τ_1'' , while the latter are close to $\tau_1 = T_1/T_{cr}$; here $\tau_1' < \tau_1$ and $\tau_1'' > \tau_1$.

The methods of additivity used for calculating the compressibility of gas mixtures may also be employed for an approximate appraisal of other properties (in particular, H and C_p of a mixture). We recommend that the method of pseudoreduced parameters also be used for this purpose.

If accurate calculations are possible (for example, by the corresponding equations), then Figs. 30-34 can serve for selecting the quantity being sought.

When calculating π and τ for hydrogen, helium and neon, better coincidence with experimentally found values will be obtained if the quantities $p_{cr}+8$ and $T_{cr}+8$ are used in all cases instead of p_{cr} and T_{cr} .

Examples

1. Find the volume of one mole of gaseous methanol at 300 °C and 200 atm.

Compare the result with the experimentally found value of $V = 114 \text{ cm}^3$.

Solution. The following values of the reduced parameters correspond to the values of the pressure and temperature indicated in the initial conditions of the example:

$$\pi = \frac{200}{78.7} = 2.54 \quad \text{and} \quad \tau = \frac{300 + 273.2}{240.0 + 273.2} = 1.12$$

From Fig. 30 we have $Z = 0.45$, and by Eq. (4.5)

$$V = 0.45 \times \frac{82.06 \times 573.2}{200} = 106 \text{ cm}^3$$

which differs from the experimentally found value by 7%.

2. What pressure should be maintained in a reservoir with a capacity of 1 m³ for it to contain 100 kg of steam at 500 °C?

Compare the result of the calculations with the data of water property tables.

Solution. The reduced temperature is $\tau = \frac{773.2}{647.3} = 1.2$. In accordance with Eq. (4.5) we have

$$p = Z \frac{RT}{V} = Z \frac{82.06 \times 773.2}{\frac{1 \times 10^6}{100 \times 10^3 / 18.02}} = Z \frac{82.06 \times 773.2}{180.02} = 352.1Z$$

consequently

$$Z = \frac{p}{352.1} = \frac{\pi p_{cr}}{352.1} = \frac{218.5}{352.1} \pi = 0.62 \pi$$

In Fig. 30 we draw a straight line through the point with the coordinates $\pi = 1$ and $Z = 0.62$ at an angle of 45°* up to its intersection with the isotherm $\tau = 1.2$. We get $Z \approx 0.75$ and $\pi \approx 1.2$.

Hence, $p \approx 1.2 \times 218.5 = 262.2 \text{ atm}$. For 500 °C and $p = 262.2 \times \frac{760}{735} = 271.1 \text{ kgf/cm}^2$ (using linear extrapolation in water property tables)

* The equation $Z = C\pi$ after taking logarithms acquires the form $\log Z = \log C + \log \pi$, which this slope of the straight line in the coordinates $\log Z$ versus $\log \pi$ (Fig. 30) corresponds to.

we find $v=0.010\ 20\ \text{m}^3/\text{kg}$ (instead of $v=1/100=0.01\ \text{m}^3/\text{kg}$). The discrepancy is 2%.

3. At what temperature will methane compressed to 140 atm have a density of $\rho=0.006\ 02\ \text{mol}/\text{cm}^3$? Use a chart of Z versus π and τ for the calculations.

Compare the result with the experimental value of $t=50\ ^\circ\text{C}$.

Solution. Since $\pi=140/45.8=3.06$ and $V=1/0.006\ 02=166.1\ \text{cm}^3/\text{mol}$, then in accordance with Eq. (4.5) we have $140 \times 166.1 = Z \times 82.06T$ or $140 \times 166.1 = Z \times 82.06T_{\text{cr}}\tau$, whence

$$Z = \frac{140 \times 166.1}{82.06 \times 191.0\tau} = \frac{1.48}{\tau}$$

Next from Fig. 30 we find the dependence of Z on τ at $\pi=3.06$ and plot it on a chart (Fig. 35). The intersection of the plotted curve with the curve $Z=1.48/\tau$ gives the sought value $\tau \approx 1.685$.

Consequently $T \approx 1.685 \times 191.0 = 321.8\ \text{K}$ ($t=48.6\ ^\circ\text{C}$), which differs from the experimental value by 1.4 K.

4. Use the method of pseudocritical parameters to find the pressure at which a mixture consisting of 34.75% ammonia and 65.25% hydrogen should be for one mole of it to occupy a volume of $196\ \text{cm}^3$ at $200\ ^\circ\text{C}$.

Compare the result of the calculations with the experimentally found value of $p=200\ \text{atm}$.

Solution. By Eq. (6.2)

$$T'_{\text{cr}} = 0.3475 \times 405.6 + 0.6525 (33.2 + 8) = 140.95 + 26.88 = 167.8\ \text{K}$$

$$p'_{\text{cr}} = 0.3475 \times 111.5 + 0.6525 (12.8 + 8) = 38.75 + 13.57 = 52.3\ \text{atm}$$

$$\tau' = \frac{200 + 273.2}{167.8} = 2.82 \quad \text{and} \quad \pi' = \frac{p}{52.3}$$

We find the pressure by the method of successive approximations.

Assume that $p=200\ \text{atm}$. Hence $\pi'=3.82$ and from Fig. 30 we have $Z \approx 0.98$, i.e.

$$V = \frac{0.98 \times 82.06 \times 473.2}{200} \approx 190\ \text{cm}^3/\text{mol}$$

which does not coincide with the value given in the initial conditions of the example.

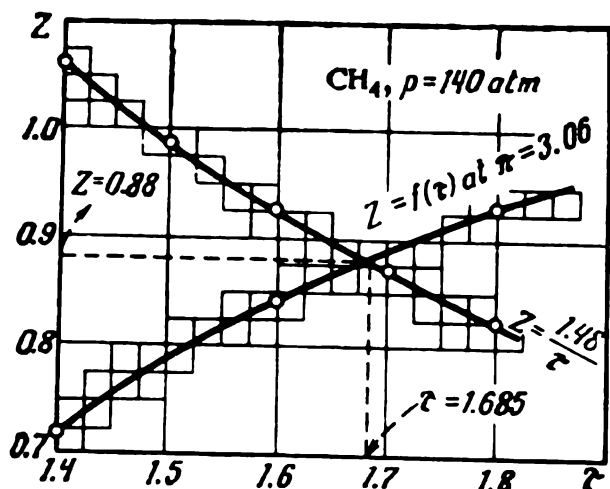


Fig. 35

Assume that $p=190$ atm. Hence $\pi'=3.63$ and from Fig. 30 we have $Z\approx 0.98$, i.e.

$$V = \frac{0.98 \times 82.06 \times 473.2}{190} \approx 200 \text{ cm}^3/\text{mol}$$

We finally assume that $p=195$ atm, which differs from the experimentally found value by 2.5%.

In view of the insufficient authenticity of the value of Z , the result of the calculations should be considered as a good one.

5. Calculate the fugacity of methane at 0°C and 200 atm and compare it with the value found in solving Problem 3 of Sec. 4.2.

Solution. On the basis of the values of $\tau=273.2/191.0=1.43$ and $\pi=200/45.8=4.37$ we find from Fig. 31 that $\gamma=0.68$. Hence $f=0.68 \times 200=136$ atm, which differs from the value found in solving the problem indicated above by 2.5%.

6. Determine the change in the enthalpy in the isothermal compression of 1 kg of steam from a very low pressure to $p=200$ kgf/cm² if $t=500^\circ\text{C}$.

Compare the result of the calculations with the exact value of $H^\circ - H = 832.9 - 774.7 = 58.2$ kcal/kg.

Solution. We convert the pressure to atmospheres, $p=200 \times \frac{735}{760} = 193.42$ atm, calculate $\pi=193.42/218.5=0.89$ and $\tau=773.2/647.3=1.2$ and from Fig. 32 determine $(H^\circ - H)/T_{cr}=1.7$, i.e. $H^\circ - H = 1100$ kcal/mol or 61.1 kcal/kg. The found value differs from the tabulated one by 5%.

7. Find C_p for methyl alcohol at $p=100$ atm and $t=340^\circ\text{C}$ and compare it with the value of $C_p \approx 30$ cal/K calculated by processing the experimental data, if at $p=1$ atm and $t=340^\circ\text{C}$ we have $C_p \approx 17.8$ for methyl alcohol.

Solution. For the values of $\pi=100/78.7=1.27$ and $\tau=613.2/513.2=1.19$ we find from Fig. 33 that $C_p - C_p^\circ \approx 8$, and therefore $C_p \approx 8 + 17.8 \approx 26$ cal/K, which differs from the value indicated in the initial conditions by 13%. Such a considerable discrepancy is possibly explained by the association of the methyl alcohol molecules.

8. (1) In accordance with the equation

$$C_p = \sum x_i (C_p)_i$$

find the heat capacity of a nitrogen-hydrogen mixture (1:3) at $t=25^\circ\text{C}$ and $p=100$ atm. Find the heat capacity of hydrogen and nitrogen at high pressures from Fig. 33. The values of $(C_p^\circ)_{298}$ for hydrogen and nitrogen are respectively equal to 6.89 and 6.96 cal/mol·K.

Compare the result with the experimentally found value of $C_p = 7.19$ cal/mol·K.

(2) May the molar heat capacity of the nitrogen-hydrogen mixture be considered an additive quantity in these conditions if the heat

capacities of hydrogen and nitrogen at $p=500$ atm and $t=100^\circ\text{C}$ are respectively 7.00 and 7.84 cal/mol·K?

Solution. (1) Since at $t=25^\circ\text{C}$ and $p=100$ atm the reduced parameters are

$$\pi_{\text{N}_2} = \frac{100}{33.5} = 2.985; \quad \tau_{\text{N}_2} = \frac{298.2}{126.1} = 2.42;$$

$$\pi_{\text{H}_2} = \frac{110}{20.8} = 4.81 \quad \text{and} \quad \tau_{\text{H}_2} = \frac{298.2}{41.2} = 7.24$$

then from Fig. 33

$$(C_p - C_p^\circ)_{\text{N}_2} = 0.90 \quad \text{and} \quad (C_p - C_p^\circ)_{\text{H}_2} \approx 0.12 \text{ cal/mol}\cdot\text{K}$$

Consequently

$$(C_p)_{\text{N}_2} = 6.96 + 0.90 = 7.86 \text{ cal/mol}\cdot\text{K}$$

$$(C_p)_{\text{H}_2} = 6.89 + 0.12 = 7.01 \text{ cal/mol}\cdot\text{K}$$

and

$$C_p = 0.75 \times 7.01 + 0.25 \times 7.86 = 7.22 \text{ cal/mol}\cdot\text{K}$$

which differs from the experimentally found value by 0.4%.

(2) Considering the heat capacity to be an additive quantity, we get

$$C_p = 0.75 (C_p)_{\text{H}_2} + 0.25 (C_p)_{\text{N}_2} = 0.75 \times 7.00 + 0.25 \times 7.84 = 7.21 \text{ cal/mol}\cdot\text{K}$$

which differs from the experimentally found value by 0.3%.

Good coincidence (within the limits of the errors of an experiment) is explained by the fact that the principle of additivity of volumes is true for the nitrogen-hydrogen mixture even at high pressures, i.e. it can be considered as an ideal solution.

9. Find the reduction in the temperature when air is throttled from $p_1=150$ atm to $p_2=0$ atm if $t_1=0^\circ\text{C}$ and $C_p^\circ \approx 6.95$ cal/K.

Compare the result of the calculation with the experimentally found value of $\Delta T=36.7$ K and with the value of $\Delta T=30.3$ K obtained when solving Problem 8 of Sec. 4.5.

Solution. The reduced parameters corresponding to the initial state are $\pi_1=150/37.2=4.03$ and $\tau_1=273.2/132.3=2.06$. Let us assume that $\tau'_1=2.0$ and $\tau''_1=2.1$. Hence from Appendix 9 we find $\gamma'_1=0.93$ and $\gamma''_1=0.95$. Therefore in accordance with Eq. (6.3) the reduction in the temperature is

$$\Delta T = \frac{4.576 \times 273.2^2 \log(0.95/0.93)}{6.95 \times 132.3 (2.1 - 2.0)} = 34.3 \text{ K}$$

which differs from the experimentally found value and from the result of solving the problem indicated above by 2.4 and 4.0 K, respectively.

Problems

1. One cubic decimetre of nitrogen is extracted from a reservoir in which $p=500$ atm and $t=20^\circ\text{C}$ and is fed into a different reservoir in which it is contained at $p=10$ atm and $t=0^\circ\text{C}$.

By how many times will the volume of the nitrogen change?

2. By how many times will the volume of ethane change if it is compressed from $p_1=20.41$ to $p_2=170.1$ atm and is simultaneously cooled from $t_1=104.4$ to $t_2=32.2^\circ\text{C}$?

Compare the result with experimental data, if the initial volume was $46.98\text{ cm}^3/\text{g}$ and the final one was $2.421\text{ cm}^3/\text{g}$.

3. What is the pressure of one mole of ammonia occupying a volume of 70.0 cm^3 at 300°C ? Compare the result of the solution with the experimentally found value of $p=488.5$ atm.

4. What temperature can a cylinder with a capacity of 3 dm^3 and containing 0.5 kg of carbon dioxide be heated to for the gauge pressure in it not to exceed 100 kgf/cm^2 ?

5. A mixture containing 74.2% by volume of methane and 25.8% by volume of nitrogen is compressed at $t=100^\circ\text{C}$ to $p=300$ atm.

Find the volume occupied by one mole of the mixture with the aid of the method of pseudoreduced parameters.

Compare the result with the experimentally obtained value of $V=106.0\text{ cm}^3/\text{mol}$.

6. Find the volume which one mole of a mixture consisting of 31.5% hydrogen, 35.2% nitrogen and 33.3% carbon dioxide will occupy at $t=0^\circ\text{C}$ and $p=400$ atm with the aid of Eq. (6.1).

Compare the result with the value of $V=59.12\text{ cm}^3/\text{mol}$.

7. Find the volume and pressure of one mole of a mixture in the conditions corresponding to Problem 5 if the calculations are performed on the basis of the assumptions of:

(1) additivity of the volumes;

(2) additivity of the pressures.

Compare the results with the values found from experimental data.

8. Under what pressure is ethylene and what is its compression factor if $\gamma=0.68$ at 137.5°C ? Perform the calculations with the aid of the data contained in Appendix 9.

9. Calculate the fugacity of methanol at $t=300^\circ\text{C}$ and $p=200$ atm. Perform the calculations with the aid of Fig. 31.

10. Find the change in the enthalpy when methane is compressed from $p_1=68$ to $p_2=170$ atm if $t=21.1^\circ\text{C}$.

Compare the result of the calculations with the experimentally found value equal to -22.1 cal/g .

11. What will the change in the temperature be in the adiabatic throttling of air from $p_1=150$ to $p_2=0$ atm if $T_1=300\text{ K}$ and $C_p=7.0\text{ cal/mol}\cdot\text{K}$?

Compare the result with the experimentally found value of 28.3 K .

12. By how much will the heat capacity of nitrogen change upon its isothermal compression from $p_1=1$ to $p_2=200$ atm if $t=100^\circ\text{C}$?

Compare the result with the experimentally obtained value of $\Delta C_p = 7.92 - 6.94 = 0.98$ cal/mol·K.

13. Discuss the possibility of using the method of pseudoreduced parameters for calculating the heat capacity on the example of a hydrogen-ammonia mixture if the results of processing experimental data on the compressibility of a mixture consisting of 34.75% ammonia and 65.25% hydrogen showed that at $t=150^\circ\text{C}$ and $p=300$ atm we have $C_p=9.58$ cal/mol·K.

Assume that at $t=150^\circ\text{C}$ we have $C_p^\circ=7.79$ cal/mol·K. The error in calculations is estimated to be 1-4%.

14. Find the reduction of the temperature in throttling steam from $p_1=20$ kgf/cm² and $t_1=300^\circ\text{C}$ to $p_2=1$ kgf/cm² with the aid of Eq. (6.3).

Compare the result of the solution with calculations according to an H - S diagram.

15. Determine the Joule-Thomson coefficient for methane at $p=50$ atm and $t=100^\circ\text{C}$ with the aid of Fig. 34 if $C_p=10.0$ cal/mol·K.

Compare the result with the values of 0.230-0.242 found by processing the experimental data.

6.2. LIQUID-VAPOUR EQUILIBRIUM

A number of charts and equations can be used for an approximate assessment of the thermodynamic properties of a liquid and vapour in equilibrium. Thus, the order of the values of the boiling point and saturated vapour pressure can be determined with the aid of Fig. 36 showing the dependence of the reduced vapour pressure on the reduced boiling point. The density of a saturated vapour and a boiling liquid can be appraised according to the chart given in Fig. 37 (K is the critical point).

The average error of the calculations according to Figs. 36 and 37 is 5-15%, although sometimes it may be greater.

The heats of vaporization can be calculated with the aid of the Meissner diagram (Fig. 38) or the *Watson equation*

$$\frac{\Delta H_{\text{vap}}}{(\Delta H_{\text{vap}})_1} = \left(\frac{1-\tau}{1-\tau_1} \right)^{0.38} \quad (6.4)$$

For calculations by means of Fig. 38, it is necessary to know the critical parameters and the boiling point at any pressure; for calculations according to Eq. (6.4), it is necessary to know the critical parameters and one value of the heat of vaporization, for example ΔH_{vap} at the normal boiling point.

To make the value of $(\Delta H_{\text{vap}})_{(5.3a)}$ found by Eq. (5.3a) more precise, the following relationship recommended by the author may

be used:

$$\frac{(\Delta H_{\text{vap}})_{(5.3a)}}{\Delta H_{\text{vap}}} \approx 1.01 + 1.4 \pi \quad (6.5)$$

where ΔH_{vap} is the precised value of the heat of vaporization.

Examples

1. Find the saturated vapour pressure of acetone at 181 °C and compare it with the experimentally found value equal to 20 atm.

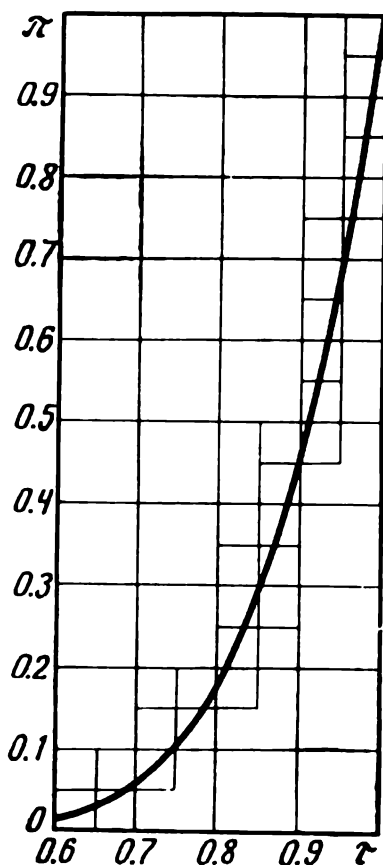


Fig. 36

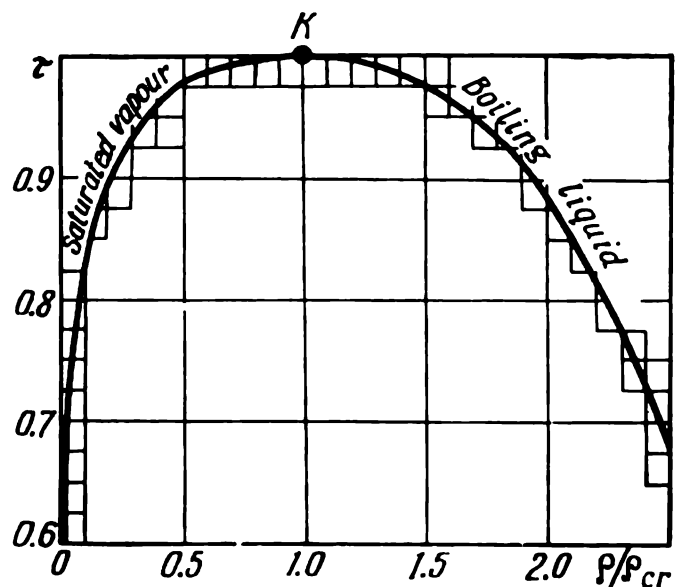


Fig. 37

Solution. Using the value $\tau = 454.2/508.2 = 0.894$, we find from Fig. 36 that $\pi \approx 0.45$. Hence $p \approx 0.45 \times 47 = 21.2$ atm, which differs from the exact value by 6%.

2. Find the density of boiling liquid ethylene and its vapour at -19.20°C if $t_{cr} = 9.6^\circ\text{C}$ and $\rho_{cr} = 0.21597$ g/cm³.

Compare the results with the experimentally found values respectively equal to 0.41313 and 0.051138 g/cm³.

Solution. We find from Fig. 37 that at $\tau = 0.898$ the reduced densities are respectively equal to $\rho^l/\rho_{cr} = 1.95$ and $\rho^g/\rho_{cr} = 0.22$.

Hence $\rho^l = 1.95 \times 0.216 = 0.421$ g/cm³ and $\rho^g = 0.22 \times 0.216 = 0.0475$ g/cm³. The found values differ from the experimentally obtained ones by 1.9 and 7.0%, respectively.

3. The heat of vaporization of octane at $t_{n.b.p.} = 125.7^\circ\text{C}$ is 70.4 cal/g . Find ΔH_{vap} at 79°C (the experimentally obtained value is 78.3) with the aid of Eq. (6.4).

Solution. The heat of vaporization is given at $\tau = \tau_{n.b.p.} = 398.9/569.4 = 0.70$. It is to be found at $\tau_1 = 352.2/569.4 = 0.62$.

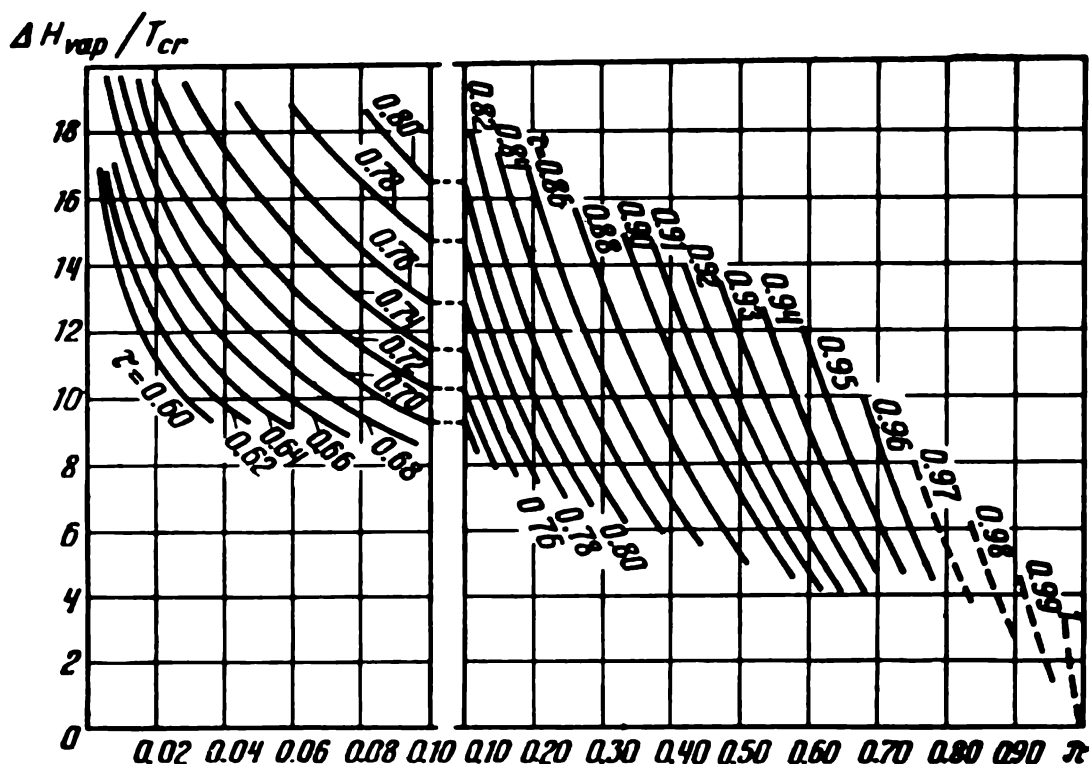


Fig. 38

Hence in accordance with Eq. (6.4) we have

$$\frac{70.4}{(\Delta H_{\text{vap}})} = \left(\frac{1 - 0.70}{1 - 0.62} \right)^{0.38} = \left(\frac{0.30}{0.38} \right)^{0.38}$$

whence

$$\Delta H_{\text{vap}} = \frac{70.4}{0.79^{0.38}} = 77.0\text{ cal/g}$$

which differs from the experimentally obtained value by 1.7%.

Problems

1. Find the boiling point of chlorine at a pressure of 20 atm. Compare the result with the exact value of $t = 65^\circ\text{C}$.
2. Determine the saturated vapour pressure of aluminium bromide at 450°C if $t_{cr} = 495^\circ\text{C}$. Compare the result with the value found by the equation proposed for the interval from 440 to 495°C :

$$\log p (\text{kgf/cm}^2) = 3.9241 - \frac{1907}{T}$$

3. Use Fig. 37 to find the equation of a straight line in the coordinates T/T_{cr} versus ρ/ρ_{cr} .

4. With the aid of the equation derived in solving Problem 3, determine the critical temperature of aluminium bromide if at 400°C we have $\rho^l = 1.846$ and $\rho^g = 0.1186$ mol/cm³, while $\rho_{cr} = 0.8875$.

Compare the result with the values found on the basis of experimental data, namely, 495 and 499°C .

Using the found values of t_{cr} , determine ρ^g at 460°C if $\rho^l = 1.565$ mol/cm³. Compare the result with the experimentally found value of $\rho^g = 0.2788$ mol/cm³.

5. Find the consumption of heat for the vaporization of 1 kg of toluene at 84°C if its normal boiling point is 110.6°C .

6. The heats of vaporization of water at $t = 200$ and 300°C are respectively 463.5 and 335.1 kcal/kg.

Find the critical temperature with the aid of Eq. (6.4) and compare it with the tabulated value.

7. Find the heat of vaporization of chloroform at $t_{n.b.p.} = 61.3^\circ\text{C}$ with the aid of Fig. 38.

Compare the result of the calculations with the values given in the initial conditions and the solution of Example 3 of Sec. 5.1.

8. The enthalpies of water and steam at $t = 200^\circ\text{C}$ and $p = 15.857$ kgf/cm² are respectively 667.0 and 203.5 kcal/kg. Determine the critical pressure. Compare the result with the tabulated value (see Appendix 8).

9. By how much will the result of calculating the heat of vaporization of phosgene change (Example 7 of Sec. 5.1) if Eq. (6.5) is used?

Chapter Seven

SOLUBILITY

7.1. INFLUENCE OF TEMPERATURE

The temperature dependence of the solubility x (mole fraction) or the dependence of the freezing point (crystallization temperature) on the composition at $p=\text{const}$ is expressed by the *Schröder equation* (*Schröder's logarithmic curve*)

$$\log x = \frac{\Delta H (T - T^\circ)}{4.576 T T^\circ} \quad (7.1)$$

It is accurate on condition that:

- (1) the solution is *ideal* within the interval from $x=1$ to x and a *pure* component freezes out from it;
- (2) the molar heat of fusion of a given component ΔH remains constant within the limits from the melting point T° to the temperature T at which its solubility is x .

A plot of $\log x$ versus $1/T$ can also be used for the calculations.

The simultaneous solution of Eqs. (7.1) for two substances yields the coordinates of the *eutectic point*; such calculations may be extended to any number of components.

In addition to calculating the equilibrium between a solid component and a saturated solution, Eq. (7.1) can be used (when the conditions indicated above are observed) for calculating the solubility of gases (see also the following section); in this case the quantities ΔH and T° will be the heat and the temperature of condensation, respectively. Equation (7.1) can also be used to find the relationship between the boiling point and the concentration of a solution.

When the laws of infinitely dilute solutions hold for a mixture, Eq. (7.1) can be simplified, and the relationship between the temperature and the concentration c in the system solution-pure component can be represented by the equation

$$T - T^\circ = Kc \quad (7.2)$$

according to which the reduction in the freezing point (the increase in the boiling point) is proportional to the concentration of the solute. The *cryoscopic constant* K is an *extrapolation* constant. Its value depends only on the nature of the solvent and the unit used to express the concentration. If the latter is expressed in moles of solute per

1000 g of solvent (molality m), then

$$K = \frac{R (T_1^\circ)^2 M_1}{1000 \Delta H_1} \quad (7.3)$$

$$m = \frac{w_2/M_2}{w_1/1000} \quad (7.4)$$

where w_2 and M_2 = weight (mass) and molecular weight (mass) of the solute

w_1 and M_1 = ditto, solvent

T_1° = solidification (boiling) point of solvent

ΔH_1 = molar heat of solidification (vaporization) of solvent.

Equation (7.2) together with Eqs. (7.3) and (7.4) is widely used for calculating M_2 .

The quantitative ratio between the phases in a heterogeneous system is determined by means of the *lever rule*, namely, the point corresponding to the total composition of the system coincides with the fulcrum of a lever equal in length to the distance between the points corresponding to the compositions of the phases (the straight connecting or tie line), while the forces acting on it are numerically equal to their masses. For this reason the latter are inversely proportional to the arms of the lever (the distances from the ends to the fulcrum).

Examples

1. The solubility of crystalline acetylene in liquid oxygen and hydrogen is as follows:

T, K	90.7	68.5
x in oxygen	6.76×10^{-6}	0.794×10^{-6}
x in nitrogen	13.6×10^{-6}	0.955×10^{-6}

Considering these solutions to be ideal ones, determine the heat of solution of acetylene in the above solvents.

Compare the result with that obtained in solving Problem 29 (Sec. 5.1).

Solution. By Eq. (7.1) we have

$$\log \frac{x_{C_2H_2}''}{x_{C_2H_2}'} = \frac{\Delta H}{4.576} \frac{T'' - T'}{T' T''}$$

hence for a solution of acetylene in oxygen

$$\log \frac{6.76 \times 10^{-6}}{0.794 \times 10^{-6}} = \frac{\Delta H (90.7 - 68.5)}{4.576 \times 90.7 \times 68.5}$$

whence

$$\Delta H = \frac{0.93013 \times 4.576 \times 90.7 \times 68.5}{22.2} = 1190$$

For a solution of acetylene in nitrogen

$$\log \frac{13.6 \times 10^{-6}}{0.955 \times 10^{-6}} = \frac{\Delta H (90.7 - 68.5)}{4.576 \times 90.7 \times 68.5}$$

whence

$$\Delta H = \frac{1.153\,54 \times 4.576 \times 90.7 \times 68.5}{22.2} = 1480$$

Since the found values appreciably differ from ΔH_{fus} for acetylene (see the solution of the problem mentioned in the initial conditions), then these solutions are not ideal ones. It is easy to see that the solubility of acetylene in oxygen and nitrogen is lower than the ideal value.

2. (1) Is it possible to judge whether a solution is ideal or not according to a plot of $\log x$ versus $1/T$?

(2) Below are given data on the composition of saturated melts of ammonium and lithium nitrates:

$t, ^\circ\text{C} \dots\dots\dots$	153.9	135.6	121.1
$x_{\text{LiNO}_3} \times 100 \dots\dots\dots$	5.74	11.40	16.98

Calculate the melting point and the heat of fusion of ammonium nitrate. The experimentally found values are respectively equal to $t_{\text{fus}} = 169.5^\circ\text{C}$ and $\Delta H_{\text{fus}} = 1460$ cal/mol. Perform the calculation graphically.

Solution. 1. It follows from Eq. (7.1) that $\partial \log x / \partial T^{-1} = -\Delta H / 4.576$. Consequently, if the points on the plot of $\log x$ versus $1/T$ are on a straight line whose continuation passes through a point with the coordinates $\log x = 0$ and $1/T^\circ = 1/T_{\text{fus}}^\circ$ and whose slope corresponds to the condition that

$$4.576 \frac{\partial \log x}{\partial (1/T)} = -4.576 \tan \alpha = \Delta H_{\text{fus}}$$

then the solution is an ideal one.

If, with account taken of the error of the experiment, even one of the above requirements is not complied with, then the solution cannot be considered as an ideal one.

2. We convert the data given in the initial conditions to $1/T$ and $\log x_{\text{NH}_4\text{NO}_3}$:

$T^{-1} \times 10^4 \dots\dots\dots$	23.41	24.46	25.36
$\log x_{\text{NH}_4\text{NO}_3} \dots\dots\dots$	-0.0257	-0.0526	-0.0808

We plot a chart of $\log x$ versus $1/T$ for ammonium nitrate (Fig. 39). We continue the straight line up to the value of $\log x = 0$ ($x = 1$). We find for NH_4NO_3 that

$$\frac{1}{T_{\text{fus}}^\circ} \times 10^4 \approx 22.55$$

whence

$$T_{fus}^{\circ} = 443.5 \text{ K } (t = 170.3^{\circ} \text{C})$$

which differs from the experimental value by 0.8 K.

From the initial conditions

$$\frac{\partial \log x}{\partial (1/T)} = -\frac{\Delta H}{4.576}$$

we get

$$\frac{4 \times 0.02}{2.8 \times 1 \times 10^{-4}} = \frac{\Delta H_{fus}}{4.576}$$

whence

$$\Delta H_{fus} = 1310 \text{ cal/mol}$$

which is less than the value indicated in the initial conditions by about 10%.

3. The freezing point of a eutectic mixture of naphthalene and benzene equals -3.6°C .

Considering this system within all the intervals of concentration to be an ideal solution, find ΔH_{fus} for naphthalene (C_{10}H_8) if for benzene (C_6H_6) we have $T_{fus} = 278.6 \text{ K}$ and $\Delta H_{fus} = 2350 \text{ cal/mol}$, and for naphthalene $t_{fus} = 80^{\circ} \text{C}$.

Compare the result with the value of $\Delta H_{fus} = 4560 \text{ cal/mol}$ for C_{10}H_8 .

Solution. From Eq. (7.1) for the curve of crystallization of benzene we have

$$\log x_{eut} = \frac{2350 (269.6 - 278.6)}{4.576 \times 278.6 \times 269.6} = -0.06155 = \bar{1}.9385$$

whence $x_{eut} = 0.868$. Consequently, for naphthalene $x_{eut} = 1 - 0.868 = 0.132$.

For the curve of crystallization of naphthalene we have

$$\log 0.132 = \frac{\Delta H_{fus} (269.6 - 353.2)}{4.576 \times 353.2 \times 269.6}$$

or

$$\bar{1}.1206 = \frac{\Delta H_{fus} \times (-83.6)}{4.576 \times 353.2 \times 269.6}$$

whence

$$(\Delta H_{fus})_{\text{C}_{10}\text{H}_8} = \frac{4.576 \times 353.2 \times 269.6 \times (-0.8794)}{-83.6} = 4580 \text{ cal/mol}$$

which differs from the experimentally found value by 0.44%.

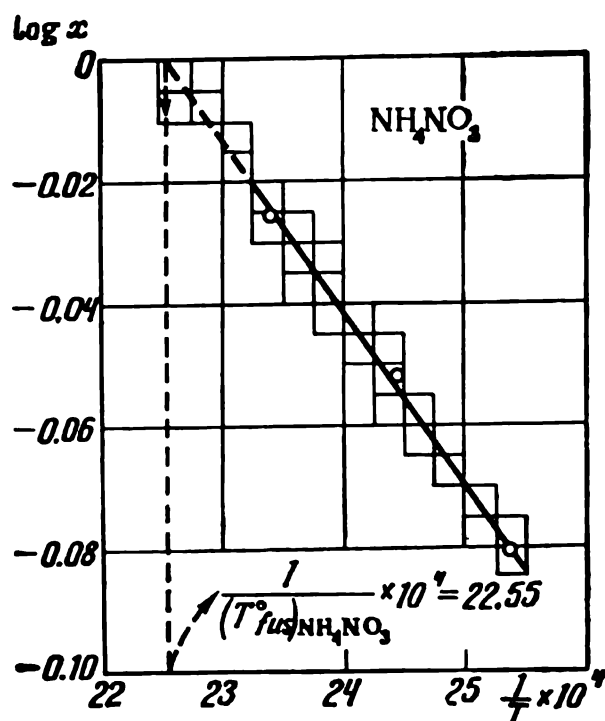


Fig. 39

4. (1) Plot a fusion diagram for the system *p*-xylene (subscript "para") and *m*-xylene (subscript "meta") if $(T_{\text{fus}})_{\text{para}}=286.5$ K, $(\Delta H_{\text{fus}})_{\text{para}}=4045$ cal/mol, $(T_{\text{fus}})_{\text{meta}}=225.4$ K and $(\Delta H_{\text{fus}})_{\text{meta}}=2765$ cal/mol.

(2) Determine the coordinates of the eutectic point.

(3) Find the consumption of heat for the melting of 1 kg of the eutectic mixture. Consider the mixture of xylenes to be an ideal solution.

Compare the results of the calculations with the experimentally found values: $t_{\text{eut}}=-53.1^{\circ}\text{C}$ and $(x_{\text{para}})_{\text{eut}}=0.133$. The dependence of the temperature of the beginning of crystallization on the composition is expressed as follows:

$x_{\text{para}} \times 100$	80.12	65.18	50.09	40.75	29.82	25.04
$t, ^{\circ}\text{C}$	4.2	-3.1	-12.0	-20.2	-30.0	-35.0
$x_{\text{para}} \times 100$	20.03	17.00	15.20	12.50	11.24	8.06
$t, ^{\circ}\text{C}$	-41.7	-46.0	-49.0	-53.1	-52.0	-51.0

Solution. 1. We find the equations corresponding to the crystallization curves of both components. In accordance with Eq. (7.1) we have

$$\log x_{\text{para}} = \frac{4045}{4.576} \left(\frac{1}{286.5} - \frac{1}{T_{\text{para}}} \right)$$

or

$$\log x_{\text{para}} = 3.088 - \frac{884.2}{T_{\text{para}}}$$

and

$$\log x_{\text{meta}} = \frac{2765}{4.576} \left(\frac{1}{225.4} - \frac{1}{T_{\text{meta}}} \right)$$

or

$$\log x_{\text{meta}} = 2.683 - \frac{604.4}{T_{\text{meta}}}$$

By choosing different values of T and introducing them into the equations obtained, we determine the composition of solutions saturated respectively with para-xylene [$p\text{-C}_6\text{H}_4(\text{CH}_3)_2$] and meta-xylene [$m\text{-C}_6\text{H}_4(\text{CH}_3)_2$]:

T, K	280	270	260	250	240	230	220	218
$\log x_{\text{para}}$	-0.070	-0.187	-0.313	-0.449	-0.596	-0.756	-0.931	-0.968
x_{para}	85.1	65.0	48.6	35.6	25.4	17.5	11.7	10.8
$t, ^{\circ}\text{C}$	6.8	-3.2	-13.2	-23.2	-33.2	-43.2	-53.2	-55.2
T, K	224	222	220					
$\log x_{\text{meta}}$	-0.015	-0.040	-0.064					
x_{meta}	96.6	91.2	86.3					
$t, ^{\circ}\text{C}$	-49.2	-51.2	-53.2					

2. According to the data obtained we plot a melting diagram (Fig. 40) on which we also plot the experimental values given in the initial conditions of the example.

The point of intersection of the crystallization curves of the components is the eutectic one. Its coordinates are $t_{\text{eut}} = -52.7^\circ\text{C}$ and $(x_{\text{para}})_{\text{eut}} \approx 0.122$, which well agree with experimental data. Thus, the assumption on the ideal nature of the solution is confirmed by the results of the calculations, which is what should be expected, since the components of the solution, being isomers, have similar properties.

3. Considering the eutectic mixture to be an ideal solution, we find that for melting one mole of it the quantity of heat needed is

$$\Delta H = 0.122 \times 4045 + 0.878 \times 2765 \approx 2921 \text{ cal/mol}$$

or, with $M_{\text{xylene}} = 106.17$, we have

$$\Delta H = 2921 \times \frac{1000}{106.17} =$$

$$= 27512 \text{ cal/kg} \approx 27.5 \text{ kcal/kg}$$

5. Use the chart plotted in solving Example 4:

(1) to calculate the relative saturation of a solution in which $x_{\text{meta}} = 0.6$ if $t = -5^\circ\text{C}$;

(2) to find the temperature which 1 kg of a solution saturated at $t = -15^\circ\text{C}$ must be cooled to for half of all the para-xylene to be in the crystalline phase. What is the composition of the solution with which the para-xylene frozen out will be in equilibrium? At what temperature will complete crystallization occur?

(3) There is a mixture of two substances whose melting diagram belongs to the type of diagram shown in Fig. 40 (a non-isomorphic mixture). To determine the composition of the mixture (or the molecular weight of the solute) the melting point T° of a pure component is measured, and then the melting point T of the mixture [see Eq. (7.2)].

What temperature should be taken for the calculations—that at which the first drop appears or that at which the last crystal disappears?

(4) In determining the freezing point of a pure solvent and a solution (in finding the molecular weight of a solute by the cryoscopic method), the liquid is supercooled and then crystallization is induced.

Will this affect the correctness of the results?

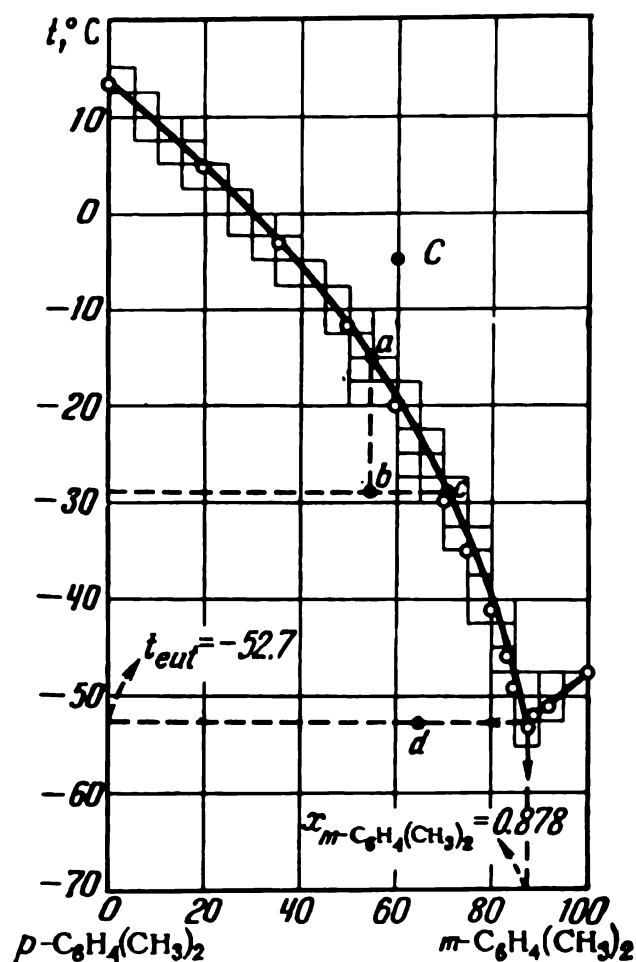


Fig. 40

(5) How would it be possible to find the composition of a solution if it is known that crystallization from it begins at -50°C ?

(6) Which quantity is greater— ΔH_{fus} for para-xylene or ΔH_{fus} for meta-xylene?

Compare the results of the calculations with the experimentally found values.

(7) Draw up the material balance for point *d* in Fig. 40 (66% of meta-xylene) if 300 grammes of the mixture are subjected to cooling.

Solution. 1. The composition of the system is determined by point *C*. At $t = -5^{\circ}\text{C}$, the concentration of a saturated solution equals about 61.5% of *p*-xylene, i.e., the relative saturation of the solution is $(40.0/61.5) \times 100 \approx 65\%$.

2. This is done with the aid of the lever rule. In Fig. 40 we draw the isotherm $t = -15^{\circ}\text{C}$ to its intersection with the curve of crystallization of *p*-xylene. We obtain the concentration of the solution saturated with *p*-xylene equal to about 45 molar per cent of this compound (point *a*). Since the molecular weight of both components is the same, then one kilogram of the solution will contain 450 g of *p*-xylene. According to the initial conditions, it is necessary to precipitate $450/2 = 225$ g; consequently, the crystalline phase must form 22.5% of the total mass, i.e. the ratio between the crystalline and the liquid phases should be $225 : 775 = 1 : 3.44$. We therefore drop a perpendicular to its intersection with the connecting line (isotherm) at the point that divides it in the ratio 1 : 3.44 (point *b*). We get $t \approx -29^{\circ}\text{C}$. The frozen out *p*-xylene will be in equilibrium with a solution containing 71% of *m*-xylene (point *c*). Complete crystallization will set in at -52.7°C .

3. It is necessary to use the temperature of disappearance of the last crystal in the calculations, since the temperature of appearance of the first drop does not depend on the composition. Actually, the melting point of the last crystal in the heating of a solid mixture coincides with the freezing point of the first crystal in cooling a liquid mixture, and this is what the value of T in Eq. (7.2) corresponds to.

4. In determining the freezing point of the pure solvent (T°), the degree of supercooling does not affect the accuracy of the results. In determining the freezing point of the solvent from the solution (T), the supercooling results in the following. When crystallization is caused by stirring, the solution changes its concentration; the result is that the freezing point will be lower than the one corresponding to the initial concentration. Hence to obtain a dependable value of T , the minimum supercooling is needed. In conducting repetitions of experiments, the supercooling each time should be the same as far as possible.

5. To find the composition of the solution, a negligible amount of meta-xylene may be added; if the temperature at which the first

crystal appears (the last crystal disappears in heating) lowers, then the point will be on the crystallization curve of para-xylene. If the temperature at which a homogeneous system transforms into a heterogeneous one is found to be higher than the initial one, then the point will be on the crystallization curve of meta-xylene.

The lever rule can also be used, since if, for example, the solution is cooled to -52°C or, which is more reliable (to avoid supercooling), a solid solution is heated to -52°C , then in the first case the solid phase will contain about 2% of the substance, and in the second one over 50%.

6. In accordance with Eq. (7.2), at low concentrations the reduction in the freezing point is proportional to the concentration. Up to $x_i=0.1$, the sections of the crystallization curves may be considered as straight lines (Fig. 40). It follows from their arrangement that the proportionality constants for para-xylene and meta-xylene are respectively equal to about 42 and 38.

The ratio of these constants [see, for example, Eq. (7.3)] is

$$\frac{(T^{\circ})_{\text{para}}^2 (\Delta H_{\text{fus}})_{\text{meta}}}{(T^{\circ})_{\text{meta}}^2 (\Delta H_{\text{fus}})_{\text{para}}} \quad \text{or} \quad \frac{42}{38} = \frac{286.3^2 (\Delta H_{\text{fus}})_{\text{meta}}}{225.3^2 (\Delta H_{\text{fus}})_{\text{para}}}$$

whence

$$\frac{(\Delta H_{\text{fus}})_{\text{para}}}{(\Delta H_{\text{fus}})_{\text{meta}}} = \frac{286.3^2 \times 38}{225.3^2 \times 42} \approx 1.461$$

i. e.

$$(\Delta H_{\text{fus}})_{\text{para}} > (\Delta H_{\text{fus}})_{\text{meta}}$$

According to experimental data

$$\frac{(\Delta H_{\text{fus}})_{\text{para}}}{(\Delta H_{\text{fus}})_{\text{meta}}} = \frac{4045}{2765} = 1.46$$

7. Point *d* corresponds to 198 g of meta-xylene and 102 g of para-xylene. Three cases should be distinguished, namely:

(a) When point *d* is reached, in accordance with the lever rule, $300 \times 0.25 = 75$ g of *p*-xylene crystals and $300 - 75 = 225$ g of the eutectic melt containing $0.878 \times 225 = 198$ g of *m*-xylene and $225 - 198 = 27$ g of *p*-xylene will be in equilibrium.

(b) In the process of crystallization of the eutectic melt, three phases will coexist: the freezing out crystals of the components and the freezing liquid. Their ratio is determined by the degree of crystallization, which, in turn, depends on the amount of heat liberated. Assume that the removal of heat (at t_{eut}) is discontinued after the liberation of 6200 cal. Since as a result of freezing of the entire melt there should be liberated $27.5 \times 225 = 61\,875$ calories of heat (27.5 is the specific heat of crystallization of the eutectic melt, see paragraph 3), the above value (6200 cal) will correspond to freezing of about one-tenth of this melt, i. e. $0.1 \times 225 \approx 23$ g. Consequently, at this moment

the system will contain $0.9 \times 225 = 202$ g of liquid (consisting of $202 \times 0.878 = 178$ g of *m*-xylene and $202 - 178 = 24$ g of *p*-xylene), $75 + 0.1 \times 27 = 78$ g of crystals of *p*-xylene and $0.1 \times 198 = 20$ g of crystals of *m*-xylene.

(c) When the isothermal removal of heat is discontinued, the system will again become a two-phase one. It will consist of 198 g of crystalline *m*-xylene and 102 g of crystalline *p*-xylene.

6. On the basis of the melting points and heats of fusion of xylenes given below, find the coordinates of the triple eutectic point:

Substance	<i>o</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene
T_{fus}° , K	247.9	225.4	286.5
ΔH_{fus} , cal	3330	2765	4045

Compare the results with the experimental data:

$$t_{eut} = -64^{\circ}\text{C}; \quad (x_{para})_{eut} = 0.095 \quad (x_{meta})_{eut} = 0.624$$

Solution. In accordance with Eq. (7.1) and with the data given above, we draw up equations for the eutectic points of three binary mixtures:

$$(\log x_{ortho})_{eut} = 2.936 - \frac{3330}{4.576 T}$$

$$(\log x_{meta})_{eut} = 2.683 - \frac{2765}{4.576 T}$$

and

$$(\log x_{para})_{eut} = 3.088 - \frac{4045}{4.576 T}$$

where T is the temperature of freezing out from solutions saturated with the corresponding component.

We determine the quantity T_{eut} as follows. We assign values to T less than $(T_{fus})_{meta}$ and by substituting them into the found equations calculate the mole fractions of all the components. After getting values of $\sum x_i$ for different temperatures, we find the temperature at which $\sum x_i = 1$ by interpolation. This will be the sought value. In this way we find $t_{eut} = -63.8^{\circ}\text{C}$, and $(x_{ortho})_{eut} = 0.292$, $(x_{para})_{eut} = 0.632$ and $(x_{meta})_{eut} = 0.074$, which well agree with experimental data.

7. The heats of solution of phenol in benzene and pyridine are respectively 2530 and -630 cal/mol. What do these figures indicate if the heat of fusion of phenol is 2730 cal/mol?

Solution. It follows from these data that phenol dissociates in benzene, while it enters into a chemical reaction with pyridine.

8. How can we explain:

(1) the difficulties encountered in exact determination of the melting point of metals, and

(2) the circumstance that glycerine and acetic acid, for which t_{fus} is respectively 19 and 16.7°C, when stored in premises in which the temperature is below the indicated values are in the liquid state (supercooling is excluded)?

Solution. 1. The cryoscopic constant, as follows from Eq. (7.3), is very great for metals, for example, for lead it is 130 ($K_{\text{Pb}}=130$). Hence even an insignificant content of impurities appreciably lowers the freezing point. This underlies the principle of preparing low-melting alloys and of choosing the charge for the blast-furnace process.

2. Since acetic acid and glycerine, being hygroscopic substances, always contain a small amount of water, their melting point is below the theoretical one [see Eq. (7.2)].

9. For a solution containing 2.2048 g of aluminium iodide and 30.98 g of aluminium bromide, the lowering of the temperature was found to be 4.37 K.

Determine the concentration of a solution of carbon tetrabromide in aluminium bromide if $T-T^\circ$ for it is 5.07 K.

Compare the result of the calculations with the experimentally found values ($w_2=1.976$ g and $w_1=29.56$ g).

Solution. We use Eq. (7.2) for the calculations, which in accordance with Eq. (7.4) becomes

$$\Delta T = K \frac{w_2/M_2}{w_1/1000}$$

For a solution of aluminium iodide in aluminium bromide we have

$$4.37 = K \frac{2.2048/407.7}{30.98/1000}$$

whence $K=25.0$.

In accordance with the found value of K for solutions of carbon tetrabromide in aluminium bromide, we have

$$5.07 = 25.0 \times \frac{w_2/331.67}{w_1/1000}$$

whence $w_2/w_1=0.06726$, which differs from the experimentally found value of $1.976/29.56=0.06685$ by 0.6%.

10. May we consider that a solution of urea [$\text{CO}(\text{NH}_2)_2$] in water up to $t_{\text{eut}}=-11.5^\circ\text{C}$ ($x_{\text{urea}}=0.125$) has the properties of an infinitely dilute solution if the freezing points of the solutions are:

$x_{\text{urea}} \times 100$. . .	0.9	1.8	2.9	3.9	5.0	6.2	7.3	8.7	10.0
$t, ^\circ\text{C}$	-0.7	-1.7	-2.9	-3.8	-4.9	-6.0	-7.1	-8.3	-9.9

Solution. Since in the given case (within the limits of the errors of the experiment) the lowering of the freezing point is proportional to the concentration ($K \approx 96$), it can be assumed that a solution of

urea in water within the range of concentrations indicated above has the properties of an infinitely dilute solution. Let us check this assumption, for which end we calculate K for the concentration expressed in molality (moles per 1000 g of solvent). For $x_{\text{urea}}=0.125$ we get

$$0.125 = \frac{w_{\text{urea}}/60.1}{w_{\text{water}}/18.0 + w_{\text{urea}}/60.1}$$

With $w_{\text{water}}=1000$ g we have $w_{\text{urea}}=477$ g.

Consequently, in accordance with Eqs. (7.2) and (7.4) we have

$$96 \times 0.125 = K \frac{477/60.1}{1000/1000}$$

whence $K=1.51$, which differs from the value

$$K = \frac{1.987 \times 273.2^2 \times 18}{1000 \times 1440} = 1.85$$

found by Eq. (7.3) by 0.34 K .

Problems

1. Find an equation for calculating the solubility of a substance in aluminium bromide considering the solution to be ideal. Calculate the concentration of a saturated solution at $t=80^\circ\text{C}$ if t_{fus} for AlBr_3 is 98°C and ΔH_{fus} for it is 2700 cal.

Compare the results with the experimentally found values of the compositions of saturated solutions of various organic compounds in AlBr_3 at $t=80^\circ\text{C}$:

Substance . .	$\text{C}_6\text{H}_5\text{NO}_2$	$o\text{-C}_6\text{H}_4\text{NO}_2\text{Br}$	$m\text{-C}_6\text{H}_4\text{NO}_2\text{Br}$	$p\text{-C}_6\text{H}_4\text{NO}_2\text{Br}$	
$x_{\text{AlBr}_3} \times 100$.	80.1	82.6	80.9	82.9	
Substance . .	$o\text{-C}_6\text{H}_4\text{CH}_3\text{NO}_2$	$m\text{-C}_6\text{H}_4\text{CH}_3\text{NO}_2$	$p\text{-C}_6\text{H}_4\text{CH}_3\text{NO}_2$	$o\text{-C}_6\text{H}_4\text{NO}_2\text{Cl}$	
$x_{\text{AlBr}_3} \times 100$.	81.7	84.8	82.9	78.2	
Substance . .	$m\text{-C}_6\text{H}_4\text{NO}_2\text{Cl}$	$p\text{-C}_6\text{H}_4\text{NO}_2\text{Cl}$	C_6H_6	$\text{C}_6\text{H}_5\text{CH}_3$	$p\text{-C}_6\text{H}_4(\text{CH}_3)_2$
$x_{\text{AlBr}_3} \times 100$	79.7	83.1	75.8	78.5	78.3

What conclusions can be drawn from the results found?

2. The melting points of o -dinitrobenzene and m -dinitrobenzene are respectively equal to 116.5 and 89.9°C . The coordinates of the eutectic point are $t=64^\circ\text{C}$ and $x_{m=\text{C}_6\text{H}_4(\text{NO}_2)_2}=0.65$.

Determine the heat of fusion of both components and compare it with the experimentally found values of $\Delta H_{\text{fus}}=5424 \pm 160$ cal for the ortho- and $\Delta H_{\text{fus}}=4155 \pm 160$ for the meta-compound.

3. In investigating the melting diagram for the system sodium pyrophosphate-sodium chloride, the following freezing points were obtained for sodium chloride:

$x_{\text{NaCl}} \times 100$	95	90
$t, ^\circ\text{C}$	784	767

Find T_{fus} and ΔH_{fus} for sodium chloride and compare them with the experimentally obtained values equal respectively to 1073 K and 7220 cal/mol.

4. The solubility of 100% sulphur dioxide in solar oil at 10 °C is 40.6 g/dm³, and at 30 °C it is 23.4 g/dm³.

Find the molar heat of solution.

5. The solubility of carbon monoxide in copper and ammonia solutions of cuprous oxide when heated from $t_1=0$ to $t_2=70$ °C decreased in one of the solutions 69.53 times.

Determine the relative reduction in solubility in heating from $t_1=0$ to $t_2=30$ °C and compare with the experimentally found value equal to about 10.9.

6. The mutual solubility of chloroacetophenone and acetophenone is expressed by the following data:

Content of chloroacetophenone, weight %	100	90	80.9	70	60	50	41.5
t , °C	53.5	48.0	42.6	35.6	29	20.5	13.1
Content of chloroacetophenone, weight %	30	20	10	0.0			
t , °C	5.9	11	15.9	20.5			

Use these data to plot a solubility diagram and determine from it:

(1) the composition of the eutectic mixture and the freezing point of the eutectic;

(2) what will happen to a small crystal of chloroacetophenone if it is thrown at 15 °C into a solution containing 75% of acetophenone;

(3) the composition and the number of phases if 1 kg of a melt containing 20% of acetophenone is cooled to $t=35$ °C (supercooling is excluded);

(4) how much acetophenone has to be added to 1 kg of chloroacetophenone for the melting point of the latter to drop to 40 °C;

(5) at what temperature a mixture consisting of 20%, 67% (a eutectic mixture) and 90% of acetophenone will begin to melt;

(6) what will happen to the mixtures indicated in (5) if they are heated to 10 °C;

(7) at what temperature will melting of the mixtures of the compositions indicated in (5) terminate;

(8) how much acetophenone has to be added to 1 kg of chloroacetophenone in order to obtain a system which at 30 °C (a) contains 50% of the liquid phase, and (b) is completely melted;

(9) how much acetophenone has to be added to 1 kg of a mixture containing 80% of chloroacetophenone for it to melt completely at about 4 °C;

(10) how much acetophenone can be dissolved in 100 kg of a solution saturated with this compound at 10 °C if the solution is heated to 15 °C;

(11) $(\Delta H_{\text{fus}})_1$ for acetophenone and $(\Delta H_{\text{fus}})_2$ for chloroacetophenone.

7. With the aid of Eq. (7.1) compare the relative solubility of two substances depending on the ratio between their melting points and heats of fusion.

8. Below are given certain data obtained in investigating crystallization in the system phenol-carbon sulphide

$T^{-1} \times 10^4$	35.33	35.85	36.08	36.81	37.54	38.50
$-\log x_{\text{C}_6\text{H}_5\text{OH}}$	0.441 29	0.5986	0.686 13	0.889 41	1.061 48	1.370 59

May this system be considered an ideal one if $T_{\text{fus}} = 313.1$ K and $\Delta H_{\text{fus}} = 2730$ cal for phenol? Perform the calculations graphically.

9. Show that if the temperature dependence of the heat of fusion is taken into account and it is assumed that

$$\frac{\partial \Delta H_{\text{fus}}}{\partial T} = C^{\text{liq}} - C^{\text{c}} = \Delta C = \text{const}$$

where C^{liq} and C^{c} are taken near the melting point, then Eq. (7.1) becomes

$$\log x = \frac{(\Delta H_{\text{fus}}) T^{\circ}}{4.576} \left(\frac{1}{T^{\circ}} - \frac{1}{T} \right) + \frac{\Delta C}{4.576} \cdot \frac{T^{\circ} - T}{T} - \frac{\Delta C}{1.987} \log \frac{T^{\circ}}{T}$$

Use the found equation to determine the concentration of a saturated solution at $t = -35^{\circ}\text{C}$ if $\Delta C \approx 3.5$. Take the data needed for the calculations from the initial conditions of Example 4. Compare the result of the calculations with the experimentally obtained value and with the result of calculations by Eq. (7.1).

10. On the basis of the results of solving Example 9 calculate the heat of fusion of aluminium bromide and compare it with the experimentally found value of $\Delta H_{\text{fus}} = 2760$ cal/mol if t_{fus} for AlBr_3 is 97.5°C .

11. When 2.6152 grammes of ethylene glycol ether were dissolved in 100 g of water, the freezing point dropped by 0.5535°C . Determine the molecular weight of the ether if ΔH_{fus} for water is 1440 cal/mol.

12. The lowering of the freezing point of a solution of 0.6298 g of sulphur dioxide in 9.7430 g of dioxane is 1.93 K.

What does the result obtained indicate if the cryoscopic constant $K_{\text{C}_6\text{H}_6\text{O}_2} = 4.83$?

13. The following results were obtained in determining the freezing point of aqueous solutions of cane sugar:

Sugar content, weight %	0.998	2.081	4.302
ΔT , K	0.0576	0.1182	0.2462

What is the error of these experimental data if it is considered that the laws of infinitely dilute solutions hold for a sugar solution of the concentrations indicated above?

14. The following data were obtained in studying the melting of cyclohexanol:

$t, ^\circ\text{C}$	23.72	25.10	26.13	27.16	29.22
p, atm	0.9869	27.03	48.23	70.40	96.58
$v^{\text{liq}}, \text{cm}^3/\text{g}$	1.0487	1.0572	1.0561	1.0573	1.0568
$v^{\text{c}}, \text{cm}^3/\text{g}$	1.0335	1.0399	1.0394	1.0379	1.0360

1. What would the freezing point of a cyclohexanol solution for which $m=0.01$ be if the experiment were conducted at a pressure of $p=60$ atm and the solution could be considered as an ideal one?

2. Would the accuracy of the results grow if the experiment were conducted at atmospheric pressure?

15. Find an expression for calculating the concentration dependence of the freezing point $(\partial T/\partial x)_{\text{eq}}$ for the freezing out of a substance from an ideal solution.

For what solvent will the crystallization curve be steeper—for toluene or hexane—if their normal boiling points are approximately equal, and $\Delta H_{\text{fus}}=1560$ cal/mol for toluene and 2950 cal/mol for hexane? Consider that the solution is an ideal one.

16. Prove that the solubility of a gas in an ideal solution diminishes with temperature elevation, at a faster rate in a good solvent than in a poor one.

7.2. INFLUENCE OF PRESSURE

The pressure dependence of the solubility at a given temperature is expressed by the equation

$$\ln \frac{x''}{x'} = \frac{V^\circ - V}{RT} (p'' - p') \quad (7.5)$$

It is strictly true only on condition that the solution is ideal and that the molar volumes of the pure solute V° and the solute in a state of a pure supercooled liquid V within the pressure interval of p' to p'' are constant.

The solubility in an ideal solution can also be found according to Raoult's law (see Sec. 8.1).

$$x = \frac{p}{p^\circ} \quad (7.6)$$

For solutions of crystalline substances p is the vapour pressure of a solid substance in equilibrium with the solution, and p° is its vapour pressure over a pure supercooled liquid. For a gas solution p° equals the pressure of the saturated vapour of the liquefied gas. If the solubility is calculated at a temperature higher than the critical temperature of the solute, then the value of p° can be approximately

found by extrapolation according to Eq. (5.3) or by a plot corresponding to this equation.

If the pressure is great, it should be replaced in Eq. (7.6) with the fugacity. To obtain more accurate results, the fugacity of a pure component must be taken at a pressure equal to the total one over a solution.

The relationship between the solubility of a poorly soluble gas and its pressure is expressed by *Henry's law* (see Chapter Eight), which the following equation corresponds to at low pressures (an ideal gas):

$$x_2^{lq} = \frac{p_2}{k} \quad (7.7)$$

where k is Henry's coefficient.

For a real solution, the concentration of the dominating component may be calculated by Eq. (7.6), and that of the substance present in a very small amount by Eq. (7.7).

The solubility of a component of a mixture is proportional to its partial pressure.

If the pressure is great, then the pressure in Eq. (7.7) must be replaced with the fugacity, while for a gas mixture the fugacity of a component of the mixture should be used (see Sec. 4.2).

To calculate the solubility of a poorly soluble gas that is under a great pressure, the *Krichevsky-Kazarnovsky equation* is used, namely,

$$\ln \frac{f_2^g}{x_2^{lq}} = \ln k + \frac{\bar{V}_2^* (p - p_1^0)}{RT} \quad (7.8)$$

where f_2^g = fugacity of the dissolved gas at a pressure equal to the total pressure p

\bar{V}_2^* = apparent partial molar volume of the dissolved gas upon infinite dilution (it is assumed to be independent of the pressure)

p_1^0 = vapour pressure of the pure solvent

k = Henry's coefficient.

If the interaction of the dissolved gases may be neglected, then the result will be the more accurate, the closer x_2^g is to unity. The value of f_2^g is usually calculated according to the fugacity rule (4.19). If a pure gas is dissolved and the vapour pressure of the solvent is not great, the quantity p_1^0 may be neglected and f_2^g considered to be the fugacity of the pure gas.

Examples

1. Find the solubility of naphthalene in benzene at $t=50^\circ\text{C}$ and $p=400$ atm if the molar volume of solid naphthalene is 112 and that of liquid supercooled naphthalene is 128 cm³. Consider the solution

of naphthalene in benzene to be an ideal one, and the volumes to be independent of the pressure. Take the heat of fusion of naphthalene equal to 4560 cal/mol, and $t_{\text{fus}}=80^\circ\text{C}$.

Solution. By Eq. (7.5) for naphthalene (C_{10}H_8) we get

$$\log \frac{x''}{x'} = \frac{112-128}{2.303 \times 82.06 \times 323.2} (400-1)$$

We find x' by Eq. (7.1)

$$\log x' = \frac{4560 (323.2-353.2)}{4.576 \times 323.2 \times 353.2} = -0.26188 = \bar{1}.7381$$

and $x'=0.547$. Consequently

$$\log x'' = (-0.26194) + \frac{(-16) \times 399}{2.303 \times 82.06 \times 323.2} = -0.3665 = \bar{1}.6335$$

and $x''=0.430$.

Hence an increase in the pressure from 1 to 400 atm causes the solubility to lower by more than 20%.

2. The solubility of methane in xylene at $t=-20^\circ\text{C}$ and $p=50$ mm Hg is 0.05 volume (reduced to standard conditions) per volume of a solvent.

Determine the solubility (in the same units) at $t=-20^\circ\text{C}$ and $p=700$ mm Hg and compare the result with the experimentally found value of $x_{\text{CH}_4}^g=0.68$.

Solution. In accordance with Eq. (7.6) for methane we have

$$\frac{(x^g)_{p'}}{(x^g)_p} = \frac{p'}{p}$$

Since the ratio of the concentrations is contained in the above expression, then

$$\frac{(x^g)_{p'}}{0.05} = \frac{700}{50}$$

whence $x^g=0.70$, which differs from the experimentally found value by 2.9%.

3. Prove that the solubility of a gas in an ideal solution related to the volume of the solution will at the given pressure be inversely proportional to the molar volume of the solvent.

Solution. Since follows from Eq. (7.6) that at the given pressure x_2^{liq} will be the same, then the solubility related to a unit of volume of the solution will be greater with a decreasing molar volume of the solvent.

4. Find the solubility of nitrogen in ethyl alcohol at $t=25^\circ\text{C}$ and $p=1$ atm and compare it with the experimentally obtained value equal to 0.1312 m³ in standard conditions per m³ of alcohol. Use the following values of the saturated vapour pressure of nitrogen:

$p_{t=-157.6}=20$ and $p_{t=-148.3}=30$ atm. Assume that the density of the alcohol is 0.789 g/cm^3 .

Solution. We determine the value of $p_{t=25}$ by extrapolation using Eq. (5.3a):

$$\log \frac{30}{20} \approx \frac{\Delta H_{\text{vap}}}{4.576} \left[\frac{(-148.3) - (-157.6)}{115.6 \times 124.9} \right]$$

whence

$$\Delta H_{\text{vap}} = \frac{4.576 \times 115.6 \times 124.9 \times 0.17609}{9.3} = 1250$$

Consequently

$$\log \frac{p_{t=25}}{30} \approx \frac{1250}{4.576} \left[\frac{298.2 - 124.9}{298.2 \times 124.9} \right]$$

whence $\log p_{t=25} = 1.477 + 1.271 = 2.748$ and $p_{t=25} = 560$ atm.

Finally, by Eq. (7.6)

$$x_{N_2} = \frac{1}{560} \approx 0.00179$$

instead of the experimentally found value

$$x_{N_2} = \frac{0.1312/22.4}{0.1312/22.4 + 1000 \times 0.789/46.07} = \frac{0.00585}{0.00585 + 17.13} = 0.00034.$$

The reason for such a considerable discrepancy between the calculated and the experimentally found values is the non-ideal solution and the approximate nature of the extrapolation of the pressure.

5. Determine the solubility of ethane in an ideal solution at $p=1$ atm and $t=35^\circ\text{C}$ if the following equation can be used for the temperature dependence of the saturated vapour pressure of ethane:

$$\log p = 4.67281 - \frac{1030.628}{312.233 + t}$$

Compare the result of the calculations with the following experimental data:

Solvent	$\text{C}_2\text{H}_5\text{OH}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	C_7H_{16}
Normal volume/volume of solvent	1.8968	2.6902	3.8498

The densities of the above solvents may be taken equal to 0.789 , 0.899 and 0.684 g/cm^3 , respectively.

Solution. We find p_{308} according to an equation of $p=f(t)$:

$$\log p_{308} = 4.67281 - \frac{1030.628}{312.233 + 35} = 1.705 \quad \text{and} \quad p_{308} = 50.7 \text{ atm.}$$

Since the properties of ethane and the solvents listed above are close, we use Eq. (7.6) for the calculations:

$$x_{\text{C}_2\text{H}_6} = \frac{1}{50.7} \approx 0.0197$$

According to the experimental data given above. the solubility has the following values:

$$\text{in alcohol } x_{\text{C}_2\text{H}_6} = \frac{1.8968/22.4}{1.8968/22.4 + 1000 \times 0.789/46.07} = 0.00491$$

$$\text{in ethyl acetate } x_{\text{C}_2\text{H}_6} = \frac{2.6902/22.4}{2.6902/22.4 + 1000 \times 0.899/88.14} = 0.0116$$

$$\text{in heptane } x_{\text{C}_2\text{H}_6} = \frac{3.8498/22.4}{3.8498/22.4 + 1000 \times 0.684/100.2} = 0.0245$$

It follows from the results of the calculations that in a first approximation solutions of ethane in heptane may be considered as ideal ones; the discrepancies between the experimental and the calculated values are beyond the accuracy limits of both, since extrapolation beyond t_{cr} was very small, while an account taken of the non-ideal nature of the ethane vapours at $p=50.7$ atm would not have given a considerable improvement of the results.*

The lower solubility in alcohol and ethyl acetate indicates the positive deviation from Raoult's law.

6. 100 m³ in standard conditions of a gas mixture consisting of 28% of carbon dioxide, 0.2% of hydrogen sulphide, 4% of carbon monoxide, 50.8% of hydrogen and 17.0% of nitrogen are fed into a scrubber for washing off the carbon dioxide. The water enters the scrubber at 15°C; scrubbing is conducted at $p=20$ atm.

Determine the theoretical consumption of water, the amount and the composition of the purified gas if 0.6% of the carbon dioxide should remain after washing. The solubility of the components of the gas mixture expressed in the volume of the gas reduced to $t=0^\circ\text{C}$ and $p=760$ mm Hg per volume of water at the given temperature if the partial pressure of the given component is 760 mm, is as follows:

Gas	CO ₂	H ₂ S	CO	H ₂	N ₂
Solubility	1.019	2.913	0.025 43	0.018 83	0.016 82

Solution. The amount of carbon dioxide to be extracted is determined by the equation

$$\frac{28.0 - x}{100 - x} \times 100 = 0.6$$

whence $x=27.57$ m³ in standard conditions.

The partial pressure of the CO₂ is $0.28 \times 20 = 5.6$ atm and its solubility is $5.6 \times 1.019 = 5.706$ m³ (in standard conditions) per m³ of H₂O.

Consequently the consumption of water is $27.57/5.706 = 4.83$ m³.

[In actual conditions the consumption of water will be greater, since saturation is not achieved (owing to the low rate of dissolving, the imperfect nature of the counterflow in the scrubber, etc.).]

* According to Fig. 31 at $p=50.7$ atm ($\pi=1.05$) and $T=308$ K ($\tau=1.01$) we have $\gamma \approx 0.65$, i.e. the fugacity differs from the pressure by 35%.

The following amounts of gases (in standard conditions) can be dissolved in 4.83 m³ of water:

$$\begin{array}{rcl}
 & & 27.57 \text{ m}^3 \text{ of CO}_2 \\
 2.913 \times 4.83 \times 20 \times 0.002 & = & 0.56 \text{ m}^3 \text{ of H}_2\text{S} \\
 0.02543 \times 4.83 \times 20 \times 0.040 & = & 0.10 \text{ m}^3 \text{ of CO} \\
 0.01883 \times 4.83 \times 20 \times 0.508 & = & 0.92 \text{ m}^3 \text{ of H}_2 \\
 0.01682 \times 4.83 \times 20 \times 0.170 & = & 0.28 \text{ m}^3 \text{ of N}_2 \\
 \hline
 \text{Total} & & 29.43 \text{ m}^3
 \end{array}$$

Consequently, all the hydrogen sulphide (0.20 m³) will dissolve, and the gas leaving the scrubber will have the following composition (in standard conditions):

$$\begin{array}{rcl}
 28 - 27.57 & = & 0.43 \text{ m}^3 \text{ of CO}_2 \\
 4 - 0.10 & = & 3.90 \text{ m}^3 \text{ of CO} \\
 50.8 - 0.92 & = & 49.88 \text{ m}^3 \text{ of H}_2 \\
 17.0 - 0.28 & = & 16.72 \text{ m}^3 \text{ of N}_2 \\
 \hline
 \text{Total} & & 70.93 \text{ m}^3
 \end{array}$$

or 0.6% of CO₂, 5.50% of CO, 70.3% of H₂ and 23.6% of N₂.

7. List the methods of removing a gas from a liquid.

Solution. It follows from Eq. (7.1) that heating can be used—the formation of real solutions for most gases is also attended by heat liberation (owing to a relatively great heat of condensation). In accordance with Eq. (7.7) it is possible to use evacuation and (or) pass an inert gas through the solution (the latter principle underlies the liberation of a gas on solid porous substances introduced into a solution). A combination of heating and evacuation is naturally more effective. It is used, for example, in the melting of a metal in a vacuum.

8. What conclusion on the dependence of the solubility on the pressure and composition of a gas can be arrived at according to the data

Table 10

$p, \text{ kgf/cm}^2$	5	10	15	20	25	30
CO ₂ , %						
100	7.97	16.18	20.9	25.5	29.7	32.6
76.8	6.57	12.7	15.9	19.3	—	24.5
49.0	—	—	3.93	7.59	12.9	—
31.6	2.32	5.06	6.24	8.26	—	10.8

obtained in studying the solubility in water of pure carbon dioxide and carbon dioxide from its mixtures with hydrogen ($t=0^\circ\text{C}$, the volume of the CO_2 is expressed in m^3 in standard conditions per m^3 of water) (Table 10).

Solution. The pressure dependence of the solubility cannot be expressed by Eq. (7.7), since the solubility grows at a slower rate than the pressure. In addition, at an identical pressure the solubility of pure CO_2 and of CO_2 from mixtures of various compositions is not the same, i.e. Dalton's law cannot be applied.

If the fugacity of pure carbon dioxide and of carbon dioxide from mixtures is calculated for the pressure indicated above, using for this purpose, for example, Eq. (4.3) and the fugacity principle (4.19), then the results obtained (see Fig. 41) make it possible to draw the conclusion that up to $p=30\text{ kgf/cm}^2$ the values of the solubility within the limits of the errors of the experiment are arranged on a common straight line. Consequently, when f_{CO_2} and f_{CO} have equal values,

the solubilities are also equal. The coincidence of the solubility of CO_2 from a mixture with that of pure CO_2 at the same fugacity is a result of the circumstance that the pressure is not great, and the second term of the right-hand part of Eq. (7.8) may be discarded.

9. The solubility q of carbon monoxide in one gramme of CH_3OH is expressed by the following data:
at $t=90^\circ\text{C}$

p , atm	50	100	150	200	250	300
q , cm^3	15.9	28.5	38.9	48.2	55.8	62.1

at $t=140^\circ\text{C}$

p , atm	86	90	145	291
q , cm^3	27.8	29.4	45.8	70.0

Find the pressure dependence of the solubility of carbon monoxide in methanol if at 90°C for CH_3OH we have $p \approx 2.5$, and at 140°C we have $p=10.63\text{ atm}$. At the latter temperature, the presence of methanol in the gaseous phase should be taken into consideration.

The content of methanol in carbon monoxide at 140°C is expressed by the following data:

p , atm	86	90	145	291
$x_{\text{CH}_3\text{OH}}$	0.113	0.107	0.075	0.037

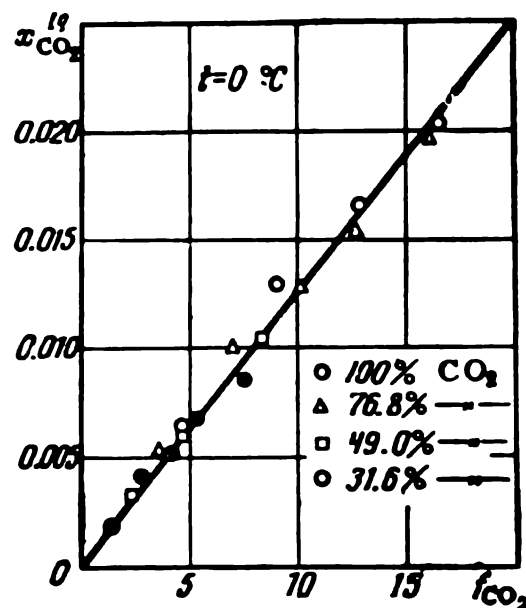


Fig. 41

Use the plot of γ versus π and τ (Fig. 31, p. 147) to calculate the fugacity of carbon monoxide.

Solution. Having calculated the values of f_{CO}^g and plotted the values of $\log (f_{\text{CO}}^g/x_{\text{CO}}^{\text{lg}})$ for $t=90^\circ\text{C}$ and $\log [(f_{\text{CO}}^g)^g x_{\text{CO}}^g/x_{\text{CO}}^{\text{lg}}]$ for $t=140^\circ\text{C}$ versus the pressure p , we draw straight lines and use their position to find $k=2090$ and $\bar{V}_{\text{CO}}^*=66.3\text{ cm}^3$ for $t=90^\circ\text{C}$, and $k=1670$ and $\bar{V}_{\text{CO}}^*=85.6$ for $t=140^\circ\text{C}$ (Fig. 42).

Consequently, for the temperatures $t=90$ and $t=140^\circ\text{C}$, Eq. (7.8) becomes, respectively

$$\log \frac{f_{\text{CO}}^g}{x_{\text{CO}}^{\text{lg}}} = 3.320 + 0.000\,966\,p$$
$$\frac{(f_{\text{CO}}^g)^g x_{\text{CO}}^g}{x_{\text{CO}}^{\text{lg}}} = 3.223 + 0.001\,096\,(p - 10.6)$$

Problems

1. The pressure dependence of the concentration (solubility) q of a saturated solution of mannitol $[\text{CH}_2\text{OH}\cdot(\text{CHOH})_4\cdot\text{CH}_2\text{OH}]$ at 25°C is expressed by the following data:

p , atm	1	500
q , g per 100 g of solution	5.59	5.31

Find the change in the volume attending the solution of one mole of mannitol in a saturated solution at 25°C .

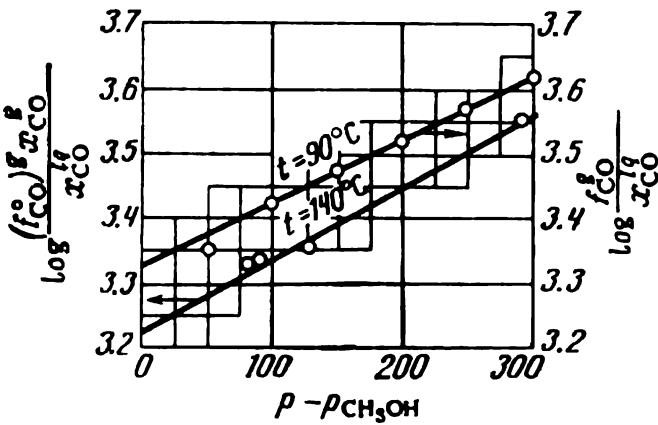


Fig. 42

2. Find the solubility of acetylene in an ideal solution at $t=0^\circ\text{C}$ and $p=1\text{ atm}$ if the vapour pressure of liquid acetylene at $t=0^\circ\text{C}$ is 26.3 atm .

Compare the result with the following data: at 0°C and 760 mm Hg , 8.5 volumes of acetylene dissolve in one volume of the 97% ethyl alcohol.

Assume that the density of the ethyl alcohol is 0.789 g/cm^3 , and that the 100% alcohol is used.

3. The vapour pressure of benzene at $t=40^\circ\text{C}$ is 182.5 , and of dichloroethane is 155.0 mm Hg . May a mixture of benzene and dichloroethane be considered an ideal solution if the following results were obtained in studying liquid-vapour equilibrium in the benzene-

dichloroethane system:

$x_{C_6H_6}^{lq}$	0.13	0.56	0.745	0.93
$p_{C_6H_6}$, mm Hg	21.9	101.0	135.0	167.2
$p_{C_2H_4Cl_2}$, mm Hg . .	134.3	70.0	41.5	12.6

Perform the calculations comparing the values of the mole fraction of one of the components computed according to the partial pressures of benzene and dichloroethane.

4. Prove that for ideal solutions a gas with a higher critical temperature (and normal boiling point) has a greater solubility than the one with a lower critical temperature.

5. How many grammes of ethylene can be dissolved in 1 dm³ of benzene at 20 °C, if the vapour pressure of liquid ethylene at $t_1=0$ °C is $p_1=40.3$ atm, and at $t_2=-10$ °C is $p_2=32.0$ atm? The density of benzene is $\rho=0.878$ g/cm³. Consider the solution of ethylene in benzene to be an ideal one.

6. Find an ideal solubility of nitrogen at $p=1$ atm and $t=20$ °C if $t_{n.b.p.}=-195.8$ °C and $(\Delta H_{vap})_{n.b.p.}=1333$ cal/mol.

Compare the result with the coefficient of absorption * of nitrogen by heptane, which at $p=1$ atm and $t=20$ °C equals 0.254. Assume that the molar volume of heptane is 146.4 cm³.

7. The solubility of sulphur dioxide in sulphuric acid up to a pressure of the dioxide of 1 atm is described by Eq. (7.7).

At $t=20$ °C and $p_{SO_2}=1$ atm, the solubility of sulphur dioxide in sulphuric acid containing from 0 to 85% of H₂SO₄ can be expressed by the equation

$$y=10.60-0.1085x$$

where y = solubility of SO₂ per 100 g of H₂SO₄

x = content of H₂SO₄ in sulphuric acid, %.

Determine the volume of SO₂ dissolved in one volume of 65% acid (a density of 1.56 g/cm³) at 20 °C and compare it with the experimentally obtained value equal to 20.80 cm³.

How many grammes of sulphur dioxide will dissolve in 1 kg of H₂SO₄ of the concentration indicated above if $p_{SO_2}=200$ mm Hg?

8. Using the data given in the initial conditions of Example 6 and the results of solving this example, find the amount and composition of the gases remaining in the wash water if in regeneration of the solution the pressure drops to $p=1$ atm.

9. A gas mixture used for synthesis of ammonia after being washed with water is processed with an ammonia solution of cuprous formate

* The absorption coefficient equals the ratio between the volume of a gas reduced to standard conditions and the volume of the solvent at the given temperature.

(for extracting carbon monoxide from the mixture), after which the solution is regenerated.

Determine an approximate consumption of the solution for washing 100 m³ of the gas, if the absorption of the CO proceeds at 0 °C and 120 atm, and the regeneration of the solution at $p=1$ atm and $t=75$ °C (in the latter case $p_{\text{NH}_3}+p_{\text{H}_2\text{O}}=550$ mm Hg).

Assume that the gas supplied for absorption has the following composition: 70.3% hydrogen, 23.6% nitrogen, 5.5% carbon monoxide and 0.6% carbon dioxide (see the

result of solving Example 6), while the absorption capacity of a solution of the given composition is expressed by the data presented in Fig. 43.

10. The following empirical formula was proposed as a result of studying the solubility of carbon dioxide in water under pressure at 25 °C:

$$V=0.755p-0.0042p^2$$

where V is the amount of carbon dioxide (in cm³) reduced to standard conditions and absorbed in 1 cm³ of water.

This equation holds for a pressure range from 10.95 to 62.9 atm.

Calculate Henry's coefficient and compare it with the value found according to the solubility of carbon dioxide in water at atmospheric pressure.

Use the values of t_{cr} and p_{cr} from Appendix 8.

11. The following approximate equation has been proposed for calculating the apparent partial molar volume:

$$\bar{V}_2^*=\bar{V}_2-\frac{2\bar{V}_2^2}{k\bar{V}_1}\left[\left(\frac{\Delta U_2}{\bar{V}_2}\right)^{\frac{1}{2}}-\left(\frac{\Delta U_1}{\bar{V}_1}\right)^{\frac{1}{2}}\right]^2$$

where $\Delta U_1/\bar{V}_1$ and $\Delta U_2/\bar{V}_2$ = internal pressures of the solvent and solute, respectively
 k = Henry's coefficient.

Use this equation to calculate the solubility of hydrogen in benzene at 25 °C and 300 atm and compare the result with the experimentally found value of $x_{\text{H}_2}=0.0708$ if $\bar{V}_{\text{H}_2}=36.3$, $\left(\frac{\Delta U}{\bar{V}}\right)_{\text{H}_2}^{1/2}=2.1$, $\left(\frac{\Delta U}{\bar{V}}\right)_{\text{C}_6\text{H}_6}^{1/2}=9.0$ cal^{1/2}/cm^{3/2}, $k=4.10^3$ and $V_{\text{C}_6\text{H}_6}=88.9$.

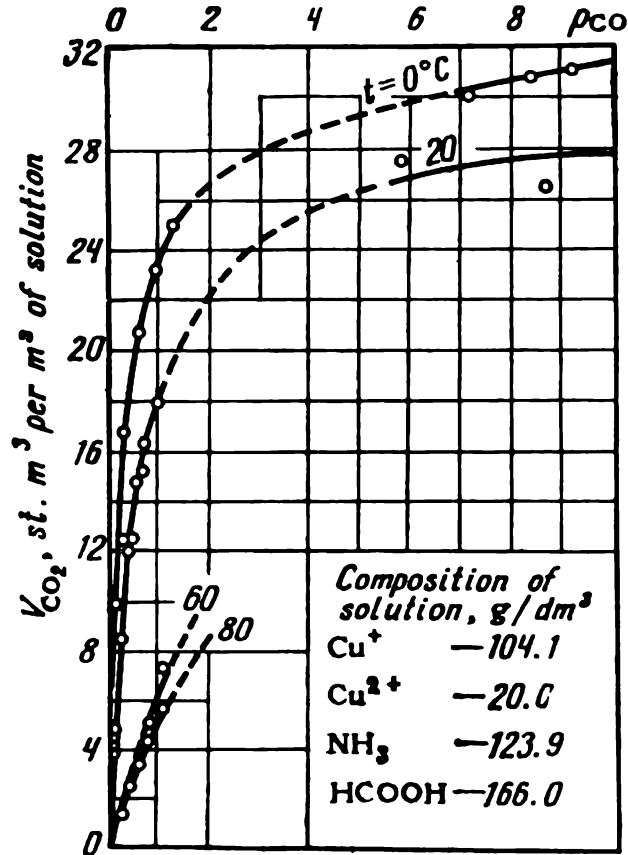


Fig. 43

7.3. MUTUAL SOLUBILITY OF LIQUIDS

Alekseev's rule, or the *rule of the straight diameter*, should be recommended for the approximate calculation of the mutual solubility (incomplete miscibility) of two liquids. According to this rule, the line passing through the middles of the tie lines connecting the compositions of conjugate solutions and through the critical solution temperature (Alekseev's point or the consolute or critical mixing temperature) is a straight one (see the phase diagram in Fig. 44).

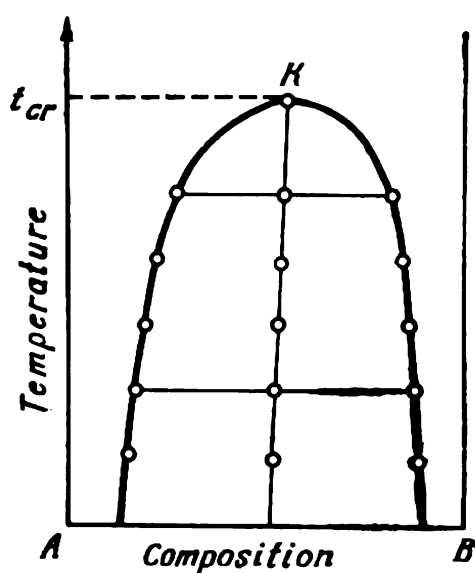


Fig. 44

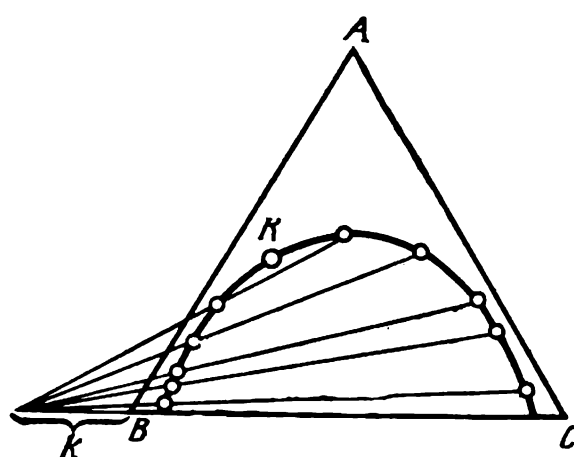


Fig. 45

This rule is the most dependable for liquids whose miscibility grows with increasing temperature. The results are the most satisfactory if the concentration is expressed in mass (weight) per cent. Alekseev's rule can also be used for an orienting assessment of the miscibility of gases at superhigh pressures.

The incomplete miscibility of three liquids in a number of cases can be approximately determined with the aid of *Tarasenkov's rule*, namely, the continuations of the tie lines connecting the compositions of the conjugated solutions intersect at one point, which lies on the continuation of the side of the triangular phase diagram on which the concentration of the incompletely miscible liquids is laid off (Fig. 45). The following equation corresponds to this rule:

$$\frac{a_2 c_1 - a_1 c_2}{a_2 - a_1} = k \quad \text{or} \quad \frac{a_1}{a_2} = \frac{c_1 - k}{c_2 - k} \quad (7.9)$$

where a_1 and a_2 = concentrations of the cosoluble component in two phases

c_1 and c_2 = concentrations of one of the incompletely miscible components

k = abscissa of the point of intersection of the continued tie lines.

The ratio between two liquid phases is determined by means of the lever rule.

In the limiting case, when two liquids are absolutely immiscible, the distribution of a substance between them is calculated by means of the *Nernst-Shilov equation* (the *distribution law*)

$$\frac{(c'')^n}{c'} = K \quad (7.10)$$

where K is the partition coefficient.

If ideal solutions are formed in both phases (there is no dissociation or association of the substances), the exponent n is equal to unity. The distribution law can be used for calculations of extraction.

Examples

1. The mutual solubility of phenol and water is expressed by the following data:

$t, ^\circ\text{C}$	20	30	40	50	55	60	65
A	8.2	8.75	9.6	11.8	13.8	16.8	23.9
B	72.1	69.9	66.8	62.6	59.2	55.1	45.8

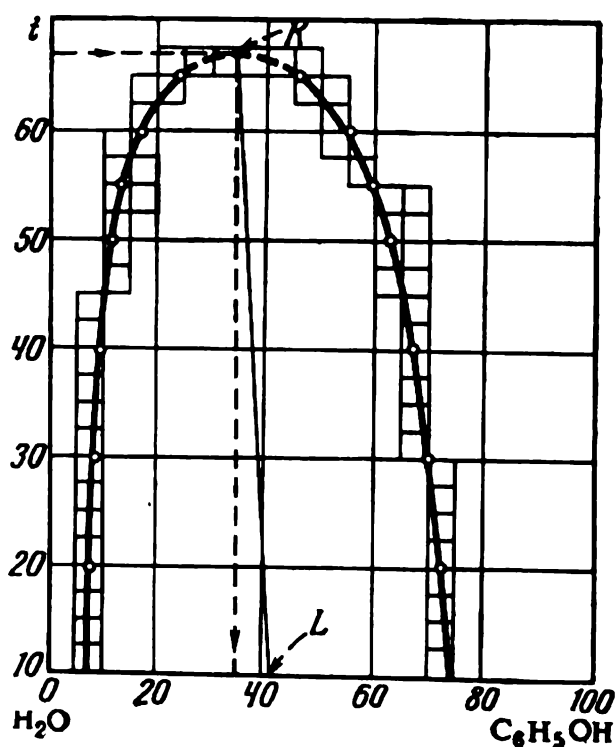


Fig. 46

where A and B are the weights per cent of phenol in saturated solutions rich in water and phenol, respectively.

Plot a phase diagram (temperature versus composition) and using Alekseev's rule, determine the composition at the critical mixing temperature if $t_{cr} \approx 67^\circ\text{C}$.

Solution. After plotting on a diagram (Fig. 46) the data given in the initial conditions, we draw a straight diameter (KL) and find that at $t_{cr} = 67^\circ\text{C}$ the concentration of the solution is about 35%.

2. The data obtained in studying the mutual solubility in the system ethyl alcohol-benzene-water at 20°C are given in Table 11.

(1) Plot a solubility diagram and check Tarasenkov's rule.

(2) Find the coordinates of the critical (mixing) temperature.

Solution. 1. After plotting a diagram according to the data given in the initial conditions (Fig. 47), we draw tie lines to their intersection with the continuation of the side of the triangle on which the content of benzene and water is laid off.

Table 11

No. of experiment	Upper phase, %			Lower phase, %		
	Alcohol	Benzene	Water	Alcohol	Benzene	Water
1	1.61	97.14	1.25	28.07	0.10	71.83
2	8.55	88.63	2.82	48.09	6.91	45.00
3	12.77	83.92	3.81	51.54	15.84	32.62
4	19.14	75.48	5.38	46.80	31.64	21.56
5	22.34	72.49	5.17	45.49	35.49	18.99
6	25.85	67.94	6.31	41.79	44.71	13.50

We discard the point of intersection of the first tie line, since owing to the low accuracy in determining very low concentrations of benzene, the error in experiment 1 is great. The remaining lines intersect at approximately a single point (point O).

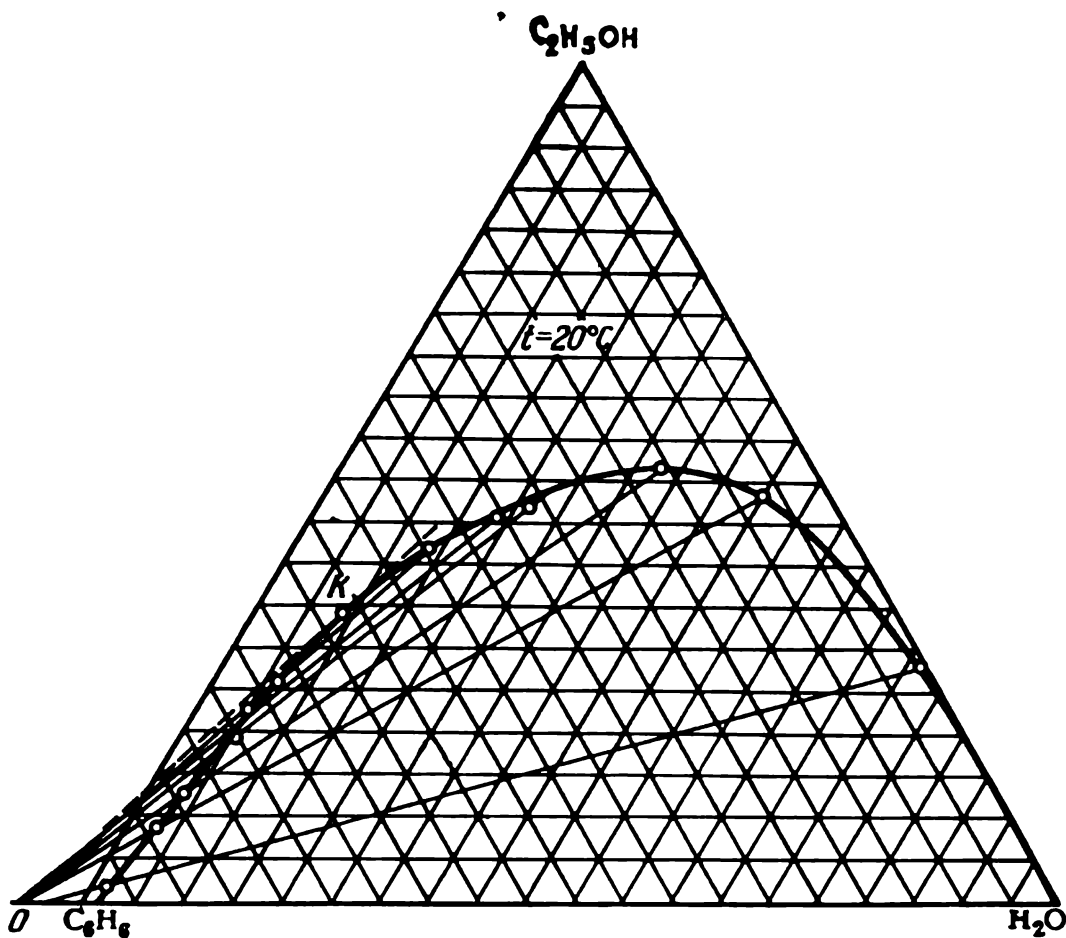


Fig. 47

2. Drawing from point O a tangent to the boundary curve, we find the coordinates of the critical (mixing) temperature K, namely, C₂H₅OH—34%, C₆H₆—57% and H₂O—9%.
3. What conclusions can be reached from the results given below in Table 12 on the distribution of ammonia between water and dichloroethane?

Table 12

Concentration of ammonia, mol/dm ³			Concentration of ammonia, mol/dm ³		
total in water, c	free NH ₃ in water, c_1	in dichloroethane, c_2	total in water, c	free NH ₃ in water, c_1	in dichloroethane, c_2
0.081 03	0.0028	0.00144	4.933	0.2139	0.116
0.0916	0.0031	0.00164	9.278	0.5120	0.276
0.552	0.0195	0.0102	11.626	0.7497	0.411
2.231	0.0851	0.0458	12.449	0.8534	0.464

Solution. The ratio c/c_2 fluctuates within the limits of 56.3 to 26.8, i.e. the deviation from the mean arithmetical value of 41.5 is $\pm 35.8\%$. The ratio c_1/c_2 is practically constant, since the maximum deviation from the mean value of 1.87 is 3.7%. Consequently, not all the ammonia participates in the distribution, but only that part of it which is in the free state.

The good coincidence of theory with experimental data is explained by the fact that the solutions of NH₃ are dilute ones; thus, even when $c=12.449$ mol/dm³, the concentration of free ammonia $c_1=0.464$ mol/dm³.

4. Prove that from Eq. (7.10) when applied to an ideal solution it follows that after n extractions the substance remaining in the initial solution is

$$x_n = a \left(\frac{KV_0}{KV_0 + V_e} \right)^n$$

where a = initial amount of substance subjected to extraction

V_0 = volume of the solution which the extracted substance is in

V_e = volume of the substance by means of which extraction is performed used per operation

K = partition coefficient of substance being extracted.

What conclusions follow from this equation?

Solution. Assume that after the first extraction x_1 grammes of the solute remain in the initial solution. Hence by Eq. (7.10)

$$\frac{x_1/V_0}{(a-x_1)/V_e} = K \quad \text{or} \quad x_1 = a \frac{KV_0}{KV_0 + V_e}$$

after the second extraction

$$\frac{x_2/V_0}{(x_1-x_2)/V_e} = K \quad \text{or} \quad x_2 = x_1 \frac{KV_0}{KV_0 + V_e} = a \left(\frac{KV_0}{KV_0 + V_e} \right)^2$$

It is obvious that for n extractions we get the sought equation.

It follows from the derived equation that for achieving the maximum extraction it is necessary to have: (a) the maximum possible diffe-

rence in solubilities; (b) the greatest possible number of operations (with the given total amount of the extracting agent), the effectiveness of the following operations rapidly diminishing; (c) the greatest possible ratio V_e/V_0 . It is impossible to achieve a complete extraction, since at any n ($\neq \infty$) we have $x_n \neq 0$.

5. Figure 48 shows the dependence of the partition coefficient showing the distribution of benzoic acid between water and benzene on its concentration in benzene at 20°C.

Determine the amount of benzoic acid in an aqueous and a benzene solutions if 1 dm³ of an aqueous solution containing 0.1 mole of the acid is mixed with 1 dm³ of benzene.

Solution. We solve the problem by the method of successive approximations. Let us denote by x' the number of moles of benzoic acid that has passed into the benzene. Hence

$$\frac{0.1 - x'}{x'} = K$$

Assuming in the first approximation that $K=0.1$, we get $x'=0.091$.

In Fig. 48 the value of $K=0.089$ corresponds to this concentration, and for this reason we pass on to the next approximation:

$$\frac{0.1 - x''}{x''} = 0.089$$

whence $x''=0.0918$.

According to Fig. 48 we finally assume that $K=0.092$, whence

$$\frac{0.1 - x'''}{x'''} = 0.092 \quad \text{and} \quad x''' = 0.0917$$

Since this value practically coincides with the concentration which the value of K has been selected for, we assume that the value obtained is the final one. Consequently, 0.0083 mole of benzoic acid will remain in the water, and 0.0917 mole will pass over into the benzene.

6. On the basis of the data given in Fig. 48, derive Eq. (7.10) and prove that benzoic acid is associated in benzene. Assume that benzoic acid has a normal molecular weight in water.

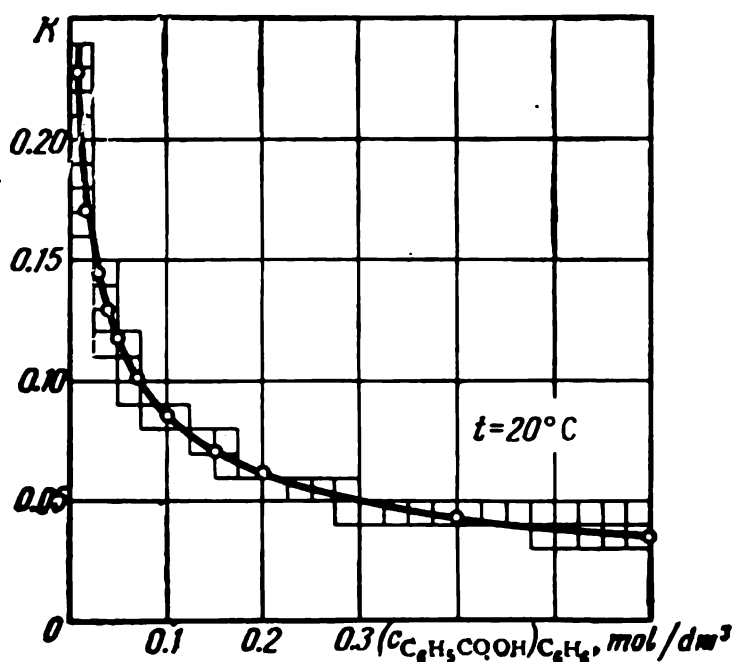


Fig. 48

Solution. Since in accordance with Eq. (7.10) we have

$$n \log c'' = \log K + \log c'$$

we calculate $\log (c_{b.ac})_{benz}$ and $\log (c_{b.ac})_{aq}$, where the subscripts "b.ac," "benz" and "aq" denote benzoic acid (C_6H_5COOH), benzene (C_6H_6) and water, respectively:

$\log (c_{b.ac})_{benz}$	—2.000	—1.699	—1.523	—1.398	—1.300	—1.155
$\log (c_{b.ac})_{aq}$	—2.642	—2.469	—2.365	—2.287	—2.232	—2.151
$\log (c_{b.ac})_{benz}$	—1.000	—0.824	—0.699	—0.398	—0.222	
$\log (c_{b.ac})_{aq}$	—2.071	—1.973	—1.907	—1.761	—1.688	

Next we plot a chart in the coordinates $\log (c_{b.ac})_{aq}$ versus $\log (c_{b.ac})_{benz}$ (Fig. 49).

Continuing the straight line obtained up to its intersection with the axis of ordinates, we find $\log K \approx 2.7$ and $K \approx 500$.

According to the slope of the straight line, we find $n = \tan \alpha = 1.82$.

Therefore Eq. (7.10) becomes

$$\frac{(c_{b.ac})_{aq}^{1.82}}{(c_{b.ac})_{benz}} = 500$$

The data obtained ($n > 1$) show that benzoic acid is associated in benzene.

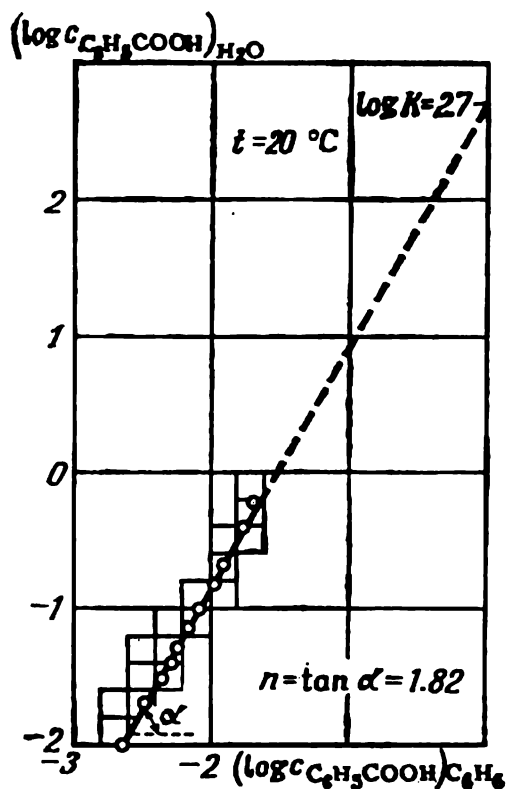


Fig. 49

Problems

1. Using the data given in Example 1 (see Fig. 46), answer the following questions:

(1) What is the limiting solubility of phenol in water and of water in phenol at 45 °C?

(2) What is greater—the differential heat of solution of water in phenol or the differential heat of solution of phenol in water?

(3) What path will the homogeneous transition from a 5% solution of phenol in water to an 80% solution of water in phenol follow provided that the temperature at the beginning and the end of the process must be 45 °C?

(4) Up to what temperature must a mixture containing 85% of water be heated for it to become homogeneous?

(5) Two test tubes at 70 °C contain the same amounts of mixtures of substances, the first of them a 45% solution, and the second a 65% one (% of phenol). In which of these two test tubes is it easier to detect stratification? Use the lever rule for solving the problem.

(6) A solution is given that becomes cloudy when cooled to 60 °C. How can the composition of the solution be determined?

(7) A homogeneous mixture consisting of 20 g of phenol and 80 g of water is cooled to 45 °C. What is the composition and the quantity of the conjugated solutions?

(8) How much water must be added to 100 g of a solution containing 80% of phenol to achieve cloudiness if $t=50$ °C?

(9) Water is poured with continuous stirring into a vessel containing 50 g of water and 50 g of phenol at 30 °C. How much water is needed for the mixture to become transparent?

(10) Phenol at 35 °C is added to a mixture of two solutions whose total weight is 100 g and which contains a water and a phenol solutions in the ratio of 2:1. How much phenol must be added for the amounts of both solutions to become equal?

2. Below are given data on the mutual solubility of water and *n*-nitrohydroquinone:

t , °C	95	105
Content of water, % by weight:		
in 1st solution	79.7	78
in 2nd solution	31.3	35

Find the composition at the critical point if $t_{cr}=120.2$ °C. Perform the calculations analytically and compare their results with the experimentally found value (58% of water).

3. On the basis of data on the mutual solubility of aniline and water it may be considered that the straight diameter in this case is a vertical line.

Determine the concentration of a saturated solution of aniline in water at $t=140$ °C if the concentration of a conjugated solution is about 82% of aniline (found by extrapolation), and at the critical (mixing) temperature the concentration of aniline is about 48.5%.

Compare the result with the experimentally found value (14.11% of aniline).

4. Investigation of the system *m*-phenylene diamine and benzene showed that at 52.5 °C, the 23.5% and 85% solutions are in equilibrium, and at 62 °C the 29.5% and 79.5% ones (weight per cent of benzene is indicated).

1. Find the equation of the straight diameter.

2. Determine whether the system will be homogeneous at 75 °C if at 68.5 °C the solubility of *m*-phenylene diamine in benzene is 30%.

5. On the basis of the results obtained in solving Example 2, find:

(1) the proportion in which benzene and water must be mixed so that the addition of alcohol will immediately result in vanishing of both layers (both layers will become identical); the amount of alcohol which would have to be added for this purpose if 1 kg of the mixture of benzene and water were taken;

(2) the composition of conjugated solutions and their proportion if 40 g of alcohol were added to 30 g each of benzene and water;

(3) how much of a mixture of water with benzene (in the proportion of 9:1) has to be added to 1 kg of alcohol before the solution becomes clouded; find the composition of the first drop of the solution formed;

(4) the interval of concentrations in which the system will be homogeneous, if a mixture of alcohol and water containing 70% of the former is added to the benzene.

6. When studying the change in the mutual solubility in the system toluene-water under the influence of alcohol (at $t=20^{\circ}\text{C}$) it was established that a mixture containing 93.88% by weight of toluene and 1.45% by weight of water is in equilibrium with a mixture containing 3.44% by weight of toluene and 50% by weight of water.

Using Eq. (7.9), determine the composition of a solution that is in equilibrium with a layer consisting of 75.24% by weight of toluene and 3.3% by weight of water if it contains 13.12% by weight of water.

Compare the results with the experimentally found data (47.38% of alcohol and 39.50% of toluene).

7. Explain the possibility of removing unreduced iron oxides from iron by adding coal to the slag over the iron (in a blast furnace) that does not mix with the latter.

8. At a concentration of iodine in water equal to 0.000 291 3, its concentration in carbon tetrachloride is equal to 0.0256.

(1) Is it possible to consider that Eq. (7.10) holds at $n=1$ up to the maximum possible concentration if the solubility of iodine in carbon tetrachloride is 0.1196, and in water is equal to 0.013 34 g per 100 g of H_2O ?

(2) Find the concentration of iodine in water if 1 dm³ of carbon tetrachloride containing 10 g of iodine is agitated with 5 dm³ of water.

9. Determine the consumption of benzene for the extraction of picric acid from 1 dm³ of an aqueous solution containing 0.3 mole of the acid if the concentration of the benzene solution must be brought up to 0.01 mol/dm³. Assume that the partition coefficient of picric acid between benzene and water is 0.705.

What is the degree of extraction?

10. The partition coefficient of iodine for water and carbon tetrachloride is 0.1115 (see the solution of Problem 8). Find the degree of extraction of iodine from 0.5 dm³ of an aqueous solution containing 0.1 g of iodine with the aid of 50 cm³ of carbon tetrachloride if extraction is performed immediately or consecutively using five identical portions.

Use the equation found in solving Example 4 for the calculations.

Chapter Eight

VAPOUR PRESSURE OF SOLUTIONS

8.1. COMPLETELY MISCIBLE LIQUIDS

The relationship between the fugacity of a component of a binary solution and its composition at $T = \text{const}$ is expressed by the *Gibbs-Duhem equation*. If Dalton's law holds for the vapours, then this equation acquires the form

$$\left(\frac{\partial \ln p_2}{\partial \ln p_1} \right)_T = \frac{d \ln x_2^{\text{lg}}}{d \ln x_1^{\text{lg}}} = - \frac{x_1^{\text{lg}}}{x_2^{\text{lg}}} \quad (8.1)$$

(For simplification, the superscript "lg" has been omitted in all the following equations.) This equation permits us to use the curve showing the dependence of the partial pressure of one of the components on the composition of the solution to plot a similar curve for the second component if at least one point is known for it. The failure to comply with Eq. (8.1) and its corollaries indicates either the inaccuracy of separate data (for example the absence of a relationship between p_1 and p_2) or the non-observance of Dalton's law (for example, as a result of association in the vapours). The latter circumstance is easily taken into account when the partial pressures are replaced by the fugacities of the components.

The following empirically found integral of Eq. (8.1) is generally used for calculations

$$\left. \begin{aligned} p_1 &= p_1^\circ x_1 \exp \left[\frac{\alpha_2}{2} (1-x_1)^2 + \frac{\alpha_3}{3} (1-x_1)^3 \right] \\ p_2 &= p_2^\circ x_2 \exp \left[\frac{\alpha_2 + \alpha_3}{2} (1-x_2)^2 - \frac{\alpha_3}{3} (1-x_2)^3 \right] \end{aligned} \right\} \quad (8.2)$$

which can be considered as sufficiently accurate.

If the vapour pressures of the pure components p_1° and p_2° are known, the constants α_2 and α_3 can be computed either on the basis of the values of the partial pressures p_1 and p_2 for one composition (by solving two equations with two unknowns), or by the equations

$$\left. \begin{aligned} \frac{\alpha_2}{2} + \frac{\alpha_3}{3} &= \ln \left[\left(\frac{\partial p}{\partial x_1} \right)_{x_1=0} + p_2^\circ \right] - \ln p_1^\circ \\ \frac{\alpha_2}{2} + \frac{\alpha_3}{6} &= \ln \left[p_1^\circ - \left(\frac{\partial p}{\partial x_1} \right)_{x_1=1} \right] - \ln p_2^\circ \end{aligned} \right\} \quad (8.3)$$

on the basis of the values of the slopes of tangents to the curve $p=f(x)$ at the points $x_1=0$ and $x_1=1$.

Both methods are not free of shortcomings. For the first one it is necessary to determine the saturated vapour pressure, which is connected with performing an analysis of the vapour phase requiring intricate apparatus and a complicated procedure. The second method requires graphical differentiation, which is not always reliable at the point of termination of the curve.

It was proposed to perform the calculations on the basis of two values of p (at $x_1=0.95$ and $x_1=0.05$) *. If the properties of a mixture do not deviate very considerably from those of ideal solutions, the constants of Eq. (8.2) can approximately be found by the equations

$$\left. \begin{aligned} \frac{\alpha_3}{3} &= -\frac{4.606}{4x_2^3-3x_1^2} \log \frac{(p_{x_1} - x_1 p_1^\circ) p_1^\circ}{(p_{x_1'} - x_1 p_2^\circ) p_2^\circ} \\ \frac{\alpha_2}{2} &= \frac{2.303}{x_1^2} \log \frac{p_{x_1'} - x_1 p_2^\circ}{x_1' p_1^\circ} - x_1 \frac{\alpha_3}{3} \end{aligned} \right\} \quad (8.4)$$

in which it is recommended to assume $x_1=0.95$ and $x_1'=0.05$ (for more accurate results respectively 0.99 and 0.01). If a mixture considerably differs from an ideal one, the following equation should be used for calculations:

$$\begin{aligned} p &= \frac{0.9p_1^\circ - 0.9p_2^\circ - p_{x_1=0.95} + p_{x_1=0.05}}{0.04275} x_1^3 + \\ &+ \frac{1.8p_2^\circ - 0.9p_1^\circ - 1.05p_{x_1=0.95} - 1.95p_{x_1=0.05}}{0.04275} x_1^2 + \\ &+ \frac{0.04275p_1^\circ - 0.04275p_2^\circ - 0.05p_{x_1=0.95} + 0.95p_{x_1=0.05}}{0.04275} x_1 + p_2^\circ \end{aligned} \quad (8.5)$$

from which the derivatives $(\partial p/\partial x_1)_{x_1=0}$ and $(\partial p/\partial x_1)_{x_1=1}$ are determined, and then Eq. (8.3) is used to calculate the constants α_2 and α_3 .

After the constants α_2 and α_3 have been found in one way or another, the values of p_1 and p_2 are found by Eq. (8.2), and then $p=p_1+p_2$.

For an *infinitely dilute solution*, the vapour pressure of the solvent is calculated by the equation

$$p_1 = p_1^\circ x_1 \quad (8.6)$$

For the solute, the relationship between the pressure and the solubility is expressed by the equation

$$p_2 = C_2 x_2 \quad (8.7)$$

* If there is an extremum beyond the limits of $x_1=0.05$ to 0.95 on the pressure curve, then the equations given below must be replaced with other ones.

If the solute is not volatile, Eq. (8.6) is generally used in the form

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 \approx \frac{n_2}{n_1} \quad (8.8)$$

For an *ideal solution*, the vapour pressure of both the solvent and the solute (if it is volatile) is calculated by Eq. (8.6).

Examples

1. The vapour pressure in the system ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), denoted by the subscripts "alc" and "di", respectively, has the following values at 50°C :

x_{alc}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
p_{alc} , mm Hg	101.2	133.0	146.5	151.9	156.4	161.6	169.5	181.3	200.4
p_{di} , mm Hg	214.5	205.5	201.5	198.9	193.9	184.8	168.7	138.2	86.0

The vapour pressure of the pure alcohol and dichloroethane is respectively 222 and 233.5 mm Hg.

Find $\alpha_2/2$ and $\alpha_3/3$ (according to the values of the derivatives at the ends of the curve of the vapour pressure) and calculate the partial and total vapour pressures at the concentrations indicated above with the aid of Eq. (8.2).

What do the results of the calculation indicate?

Solution. According to the data given above, we calculate the total pressure:

x_{alc}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
p , mm Hg	315.7	338.5	348.0	350.8	350.3	346.4	338.2	319.5	286.4

We use the values of p_{alc} , p_{di} and p to plot a chart of vapour pressure versus composition (Fig. 50). Next we draw tangents to the curve of $p=f(x_{\text{alc}})$ at the points $x_{\text{alc}}=0$ and $x_{\text{alc}}=1$. The slopes of the tangents AC and BD are equal to

$$\left(\frac{\partial p}{\partial x_{\text{alc}}}\right)_{x_{\text{alc}}=0} = \frac{360 - 233.5}{0.09} = 1405$$

and

$$-\left(\frac{\partial p}{\partial x_{\text{alc}}}\right)_{x_{\text{alc}}=1} = \frac{340 - 222}{0.17} = 694$$

In accordance with Eq. (8.3) we have

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{3} = 2.303 [\log (1405 + 233.5) - \log 222] = 1.999$$

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{6} = 2.303 \{\log [222 - (-694)] - \log 233.5\} = 1.367$$

Solution of these equations yields $\alpha_2=1.470$ and $\alpha_3=3.792$.

For $x_{\text{alc}}=0.1$ in accordance with Eq. (8.2) we have

$$p_{\text{alc}} = 222 \times 0.1 \exp (0.735 \times 0.9^2 + 1.264 \times 0.9^3)$$

or

$$\log p_{alc} = 1.346\,35 + 0.6586 = 2.0050$$

whence $p_{alc} = 101.2$ mm Hg. Correspondingly

$$p_{di} = 233.5 \times 0.9 \exp(2.631 \times 0.1^2 - 1.264 \times 0.1^3)$$

or

$$\log p_{di} = 2.322\,53 + 0.010\,88 = 2.333\,41$$

and $p_{di} = 215.0$ mm.

In a similar way we calculate the vapour pressure for the other concentrations. We get the following results:

x_{alc}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
p_{alc} , mm Hg	101.2	135.8	147.3	152.0	156.2	162.4	171.7	184.8	201.5
p_{di} , mm Hg	215.5	205.3	200.2	196.8	192.4	183.2	164.8	131.6	78.2
p , mm Hg	316.7	341.1	347.5	348.8	348.6	345.6	336.5	316.4	279.7

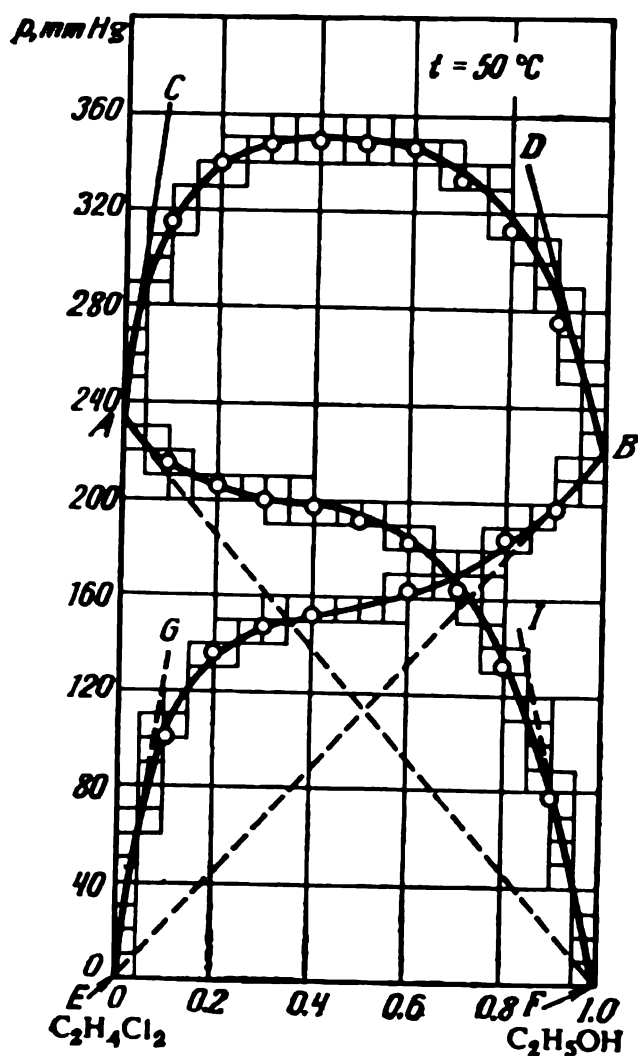


Fig. 50

We plot the calculated values of p_{alc} , p_{di} and p on a chart of p versus x (see the points in Fig. 50).

The mean discrepancy between these values and the experimentally found ones is 1.3%.

In view of the inaccuracy of graphical differentiation, enhanced by the absence of experimental points near $x_{alc} = 0$ and 1, the results of the calculations should be considered as good ones, and the experimentally found data as sufficiently reliable.

2. Prove that to check the dependability of experimental data on the vapour pressure over solutions, it is possible to use curves relating the logarithms of the activity coefficients of the components $\gamma_1 = a_1/x_1$ and $\gamma_2 = a_2/x_2$ to the composition of a solution.

Solution. Since for very dilute solutions Eq. (8.7) holds for the

solvent, and Eq. (8.6) for the solute, then the curves in the coordinates $\log \gamma_i = f(x_i)$, where $\gamma_i = p_i/p_i^\circ x_i$, should have horizontal sections in the region of low concentrations of a component and correspond to the value of $\log \gamma = 0$ for concentrations close to unity.

3. In studying liquid-vapour equilibrium in the carbon disulphide (CS₂)-benzene (C₆H₆) system, denoted by the subscripts “cd” and “ben”, respectively, the following data were obtained at 25 °C.

$x_{ben} \times 100$	0	2.11	4.68	11.53	18.24	30.02
p_{cd} , mm Hg	361.1	352.7	344.1	321.4	299.1	263.6
p_{ben} , mm Hg	0	3.5	7.1	16.0	24.0	35.1
$x_{ben} \times 100$	49.86	63.02	76.63	87.14	94.19	100
p_{cd} , mm Hg	197.4	156.6	102.5	60.2	27.9	0
p_{ben} , mm Hg	53.7	63.5	75.3	83.8	89.5	94.9

Check the mutual correspondence of these data. Use the results obtained in solving Example 2 for the calculations.

Solution. We calculate the logarithms of the activity coefficients:

$$\gamma_{cd} = \frac{p_{cd}}{p_{cd}^{\circ} x_{cd}} \quad \text{and} \quad \gamma_{ben} = \frac{p_{ben}}{p_{ben}^{\circ} x_{ben}}$$

The values obtained are as follows:

$x_{ben} \times 100$. . .	2.11	4.68	11.53	18.24	30.02
$\log \gamma_{cd}$	−0.000 66	−0.000 13	0.002 62	0.005 65	0.018 35
$\log \gamma_{ben}$	0.242 52	0.203 74	0.165 02	0.141 92	0.090 63
$x_{ben} \times 100$. . .	49.86	63.02	76.63	87.14	94.19
$\log \gamma_{cd}$	0.037 54	0.069 19	0.084 43	0.112 84	0.123 79
$\log \gamma_{ben}$	0.054 95	0.026 02	0.151 2	0.005 75	0.000 55

After plotting these data on a chart (Fig. 51), we see that they qualitatively satisfy Eq. (8.1). For quantitative checking, we reduce Eq. (8.1) to the form

$$d \ln \frac{a_1}{x_1} = - \frac{1-x_1}{x_1} d \ln \frac{a_2}{x_2}$$

or

$$\frac{d \ln \gamma_1}{dx_1} = - \frac{1-x_1}{x_1} \frac{d \ln \gamma_2}{dx_2}$$

or

$$\frac{\partial \log \gamma_1 / \partial x_1}{\partial \log \gamma_2 / \partial x_2} = - \frac{1-x_1}{x_1}$$

Calculation of the right-hand and left-hand parts of the latter equation yields

x_{cd}	0.25	0.50	0.75
$-\frac{1-x_{cd}}{x_{cd}}$	−3.0	−1.0	−0.33
$\frac{\partial \log \gamma_{cd} / \partial x_{cd}}{\partial \log \gamma_{ben} / \partial x_{ben}}$	−3.74	−1.31	−0.48

Although the data in the last line cannot be acknowledged as dependable (the inaccuracy of graphical differentiation, the scatter of the experimentally found points and the small size of the chart tell), the discrepancies between them and the data of the preceding line

are so great that the experimentally found data should be considered inaccurate.

4. (1) Show on the basis of Eq. (8.1) that for a given composition of a solution, the angles formed by a tangent to the curve of the partial pressure and by a secant connecting the point of tangency with the origin of coordinates are equal to each other.

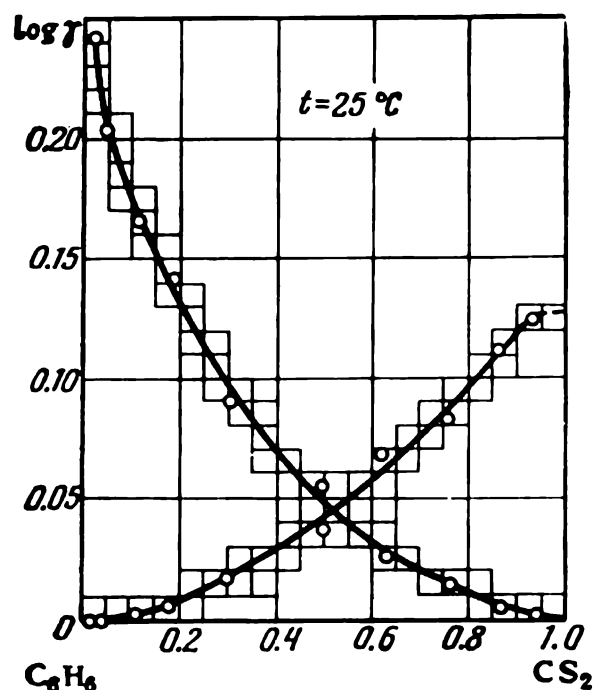


Fig. 51

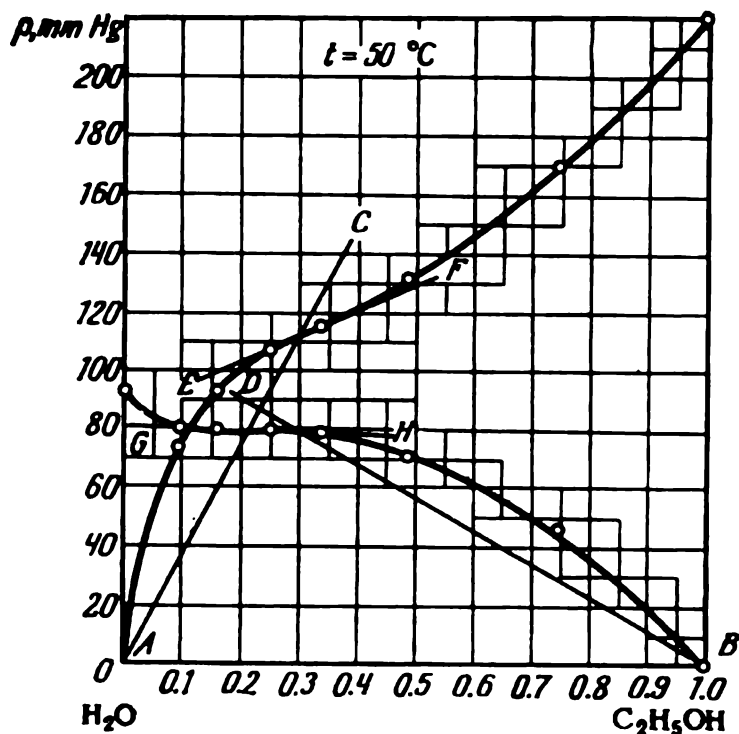


Fig. 52

(2) Use the found equation to check the mutual correspondence of the data obtained in studying the vapour pressure in the ethyl alcohol-water system at 50 °C (Fig. 52).

Solution. 1. Let us rewrite Eq. (8.1) as follows:

$$\frac{\partial \ln p_2}{\partial \ln p_1} = \frac{x_1 dx_2}{x_2 dx_1} \quad \text{or} \quad \frac{\partial p_2 / \partial x_2}{p_2 / x_2} = \frac{\partial p_1 / \partial x_1}{p_1 / x_1}$$

The rule formulated in the initial conditions of the example follows from the last equation, since the numerators of the left-hand and right-hand parts are equal to the slopes of the relevant tangents, and the denominators, to the slopes of the relevant secants.

2. For checking, choose sections of the curves with a great number of points. Draw tangents and secants to the curves at the point $x_{\text{C}_2\text{H}_5\text{OH}} = 0.30$.

Hence for water the ratio between the slope of tangent GH to that of secant DB will be

$$\frac{3}{0.40} : \frac{79}{0.70} = 0.062$$

and for alcohol the ratio between the slope of tangent EF to that of secant CA will be

$$\frac{30}{0.33} \div \frac{112}{0.30} = 0.244$$

Such a considerable discrepancy points to the low accuracy of the experimental data in this region of concentrations, since the error in graphical differentiation is not great, and it is impossible to explain the lack of coincidence by the failure of the gas mixture to comply with Dalton's law (owing to its non-ideal nature or association of the components in the vapours).

5. At 40°C the vapour pressure of dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$)—"di" and benzene (C_6H_6)—"ben" is 155.0 and 182.5 mm Hg, respectively.

(1) Plot the dependence of the total and partial vapour pressures on the composition, considering the solution to be an ideal one. What conclusions can be reached from the results of the solution if the experimental data are as follows:

$x_{\text{ben}} \times 100$. . .	7.5	13.0	18.6	25.7	34.5	46.2	56.0	64.0	69.5	74.5
p_{di} , mm Hg	.	142.3	134.3	124.8	113.0	101.6	85.0	70.0	58.0	49.8	41.5
p_{ben} , mm Hg	.	13.2	21.9	33.2	48.6	62.4	83.5	101.0	114.5	124.7	135.0
$x_{\text{ben}} \times 100$. . .	79.2	84.8	87.5	92.5	94.5					
p_{di} , mm Hg	.	32.2	24.0	18.5	12.5	9.35					
p_{ben} , mm Hg	.	145.0	154.2	160.5	167.2	171.5					

(2) Find (a) the composition of a mixture that will boil at $p=170$ mm Hg, and (b) at what pressure a mixture containing 40 mole per cent of benzene will boil.

Solution. 1. Since in an ideal solution, according to Eq. (8.6), the partial pressures are proportional to the concentrations, then by laying off p_{di}° and p_{ben}° along the axes of ordinates and drawing straight lines connecting the upper points, we construct a line of the total vapour pressure. After plotting the data given in the initial conditions on the chart, we see that within the limits of the errors of the experiment the solution may be considered as an ideal one (Fig. 53).

2. We find from the chart: (a) 54% of C_6H_6 ; (b) 167 mm Hg.

6. Plot a pressure-composition diagram (liquid and vapour) for the system considered in Example 1.

Solution. Since according to Dalton's law for the i th component of a mixture we have

$$x_i^g = \frac{p_i}{p_{\text{tot}}}$$

then, for example, in an equilibrium solution in which $x_{\text{C}_2\text{H}_5\text{OH}}^{\text{liq}}=0.50$ we have $x_{\text{C}_2\text{H}_5\text{OH}}^g = \frac{156.4}{350.3} = 0.447$.

In a similar way we can find the composition of the vapour for other compositions of the liquid. We plot a vapour curve (the dash line in Fig. 54) according to the found values of $x_{\text{C}_2\text{H}_5\text{OH}}^g$.

7. Using the charts plotted in solving Examples 1 and 6, determine:
- (1) the approximate concentration to which it may be considered that Eqs. (8.6) and (8.7) hold for the components of a solution.
 - (2) the pressure at which the condensation of a mixture will begin for which $x_{\text{C}_2\text{H}_5\text{OH}}=0.3$ and which is under a pressure of 220 mm Hg. What is the composition of the first drop of a condensate?

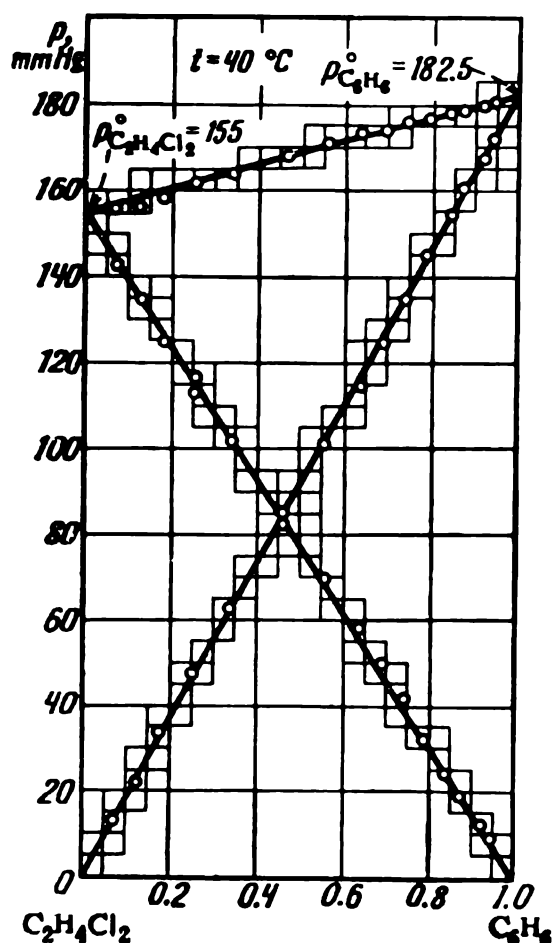


Fig. 53

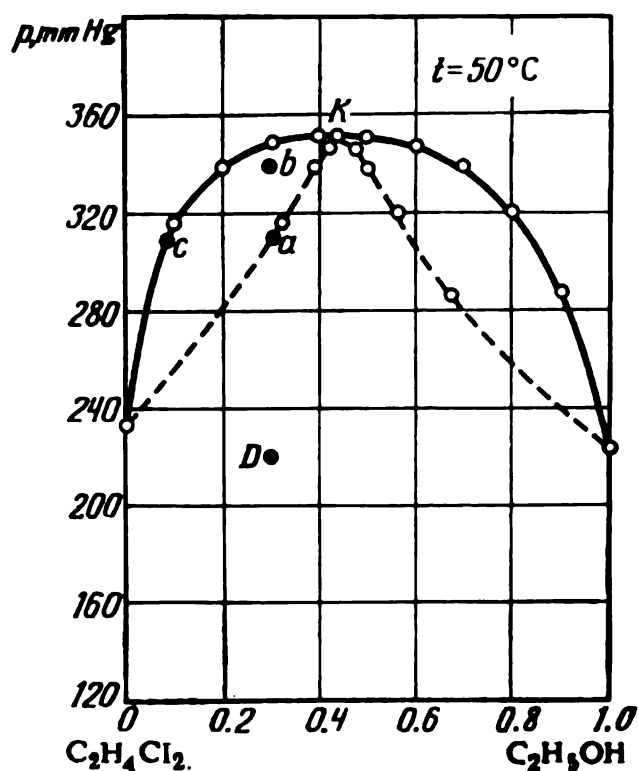


Fig. 54

(3) the pressure to which a vapour having the composition indicated in (2) should be compressed for half of it to condense.

(4) what component a constant boiling (azeotropic) mixture being distilled at $t > 50^{\circ}\text{C}$ will become enriched in if according to *Vreusky's rule* such a mixture becomes enriched with the component having a greater heat of vaporization with elevation of the temperature.

Solution. 1. Drawing lines (see Fig. 50) corresponding to Eqs. (8.6) (straight lines BE and AF) and (8.7) (straight lines EG and FI), we find that a solution of ethyl alcohol in dichloroethane may be considered an infinitely dilute one up to about $x_{\text{C}_2\text{H}_5\text{OH}}=0.04$. A solution of dichloroethane in alcohol may be considered an infinitely dilute one up to about $x_{\text{C}_2\text{H}_4\text{Cl}_2}=0.08$.

A glance at Fig. 50 shows that for the regions of the concentrations where the substance present in an excess amount (the solvent) is described by Eq. (8.6), the substance present in a smaller amount

(the solute) is described by Eq. (8.7). Figure 50 also illustrates the following fact: if the proportionality factor in Eq. (8.6) has the physical meaning of the vapour pressure of the pure solvent, then the proportionality factor in Eq. (8.7) does not have the physical meaning of the vapour pressure of the pure solute.

2. Drawing a vertical line (see Fig. 54) from the point D having the coordinates $x_{C_2H_5Cl_2}=0.7$ ($x_{C_2H_5OH}=0.3$) and $p=220$ mm Hg, we find that condensation begins at $p\approx 310$ mm Hg (point a).

For the first drop of condensate $x_{C_2H_5Cl_2}=0.92$ (point c).

3. Using the lever rule, we find that $p=340$ mm (point b).

4. Since the heats of vaporization are not given in the initial conditions of the example, let us turn to Fig. 50 to answer the question raised. It follows from the figure that at 50°C dichloroethane is a more volatile component than ethyl alcohol, therefore the boiling point of alcohol is higher than that of the dichloroethane. From this it follows, in turn, that the heat of vaporization of alcohol is greater than that of the dichloroethane [see Eq. (5.4)]. Thus, with a rise in the temperature, the point K should shift upward and to the right, which is confirmed by the experimental data. It is obvious, however, that the azeotropic mixture will only insignificantly be enriched with the alcohol.

Problems

1. The values of the vapour pressure in the methylal [$\text{CH}_2(\text{OCH}_3)_2$]-chloroform (CHCl_3) system at 35.0°C were used to find the coefficients of Eq. (8.2), namely, $\alpha_2/2=-0.8471$ and $\alpha_3/3=-0.1361$. The calculations were performed by means of Eq. (8.4) in which $x_1=0.95$ and $x'_1=0.05$.

Determine the accuracy of the calculations with the aid of the coefficients indicated above for $x_{\text{methylal}}=0.1882$ and $x_{\text{methylal}}=0.3588$ if according to experimental data the partial pressures of the components over the solution are respectively 287.7 and 307.3 mm Hg. Assume that the vapour pressure of pure methylal and chloroform is respectively 585.0 and 296.4 mm Hg.

2. At 35.1°C the vapour pressure over a mixture of acetone ($\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$) and methylal [$\text{CH}_2(\text{OCH}_3)_2$] has the following values:

x_{methylal}	0	0.05	0.95	1.0
p , mm Hg	346.6	368.2	584.6	591.4

1. Calculate the partial vapour pressures of methylal and acetone and the total vapour pressure at $x_{\text{methylal}}=0.1$ to 0.9 (at intervals of 0.1) with the aid of Eq. (8.5).

2. Plot a vapour pressure-composition diagram.

3. Assess the accuracy of the calculations if the control tests gave the following results: $p=489.5$ mm Hg at $x_{\text{methylal}}=0.4506$ and $p=530.0$ mm Hg at $x_{\text{methylal}}=0.6394$.

3. At 15 °C the saturated vapour pressures of liquid ethyl chloride and liquid diethyl ether are 837 and 362 mm Hg, respectively, and the vapour pressures of the solutions in which $x_{\text{C}_2\text{H}_5\text{Cl}}=0.196$ and 0.920 are 512 and 822 mm Hg, respectively.

Is it possible to consider that this solution at the concentrations indicated above has the properties of an infinitely dilute solution if the exact calculations give $p_{\text{C}_2\text{H}_5\text{Cl}}=772$ (at $x_{\text{C}_2\text{H}_5\text{Cl}}=0.92$) and $p_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5}=303$ mm Hg (at $x_{\text{C}_2\text{H}_5\text{Cl}}=0.196$)?

4. Show with the aid of Eq. (8.1) that when the composition dependence of the vapour pressure of a given component is a linear one, the line for the second component will also be a straight one (within the same interval of compositions).

5. Show with the aid of Eq. (8.1) that an isotherm of the total pressure cannot have any points of inflection.

6. Find the vapour pressure over a solution containing 20% by weight of *o*-xylene, 30% of *m*-xylene and 50% by weight of *p*-xylene if the solution is at 80 °C and it may be considered as ideal. The vapour pressure of the pure components should be assumed equal respectively to 108.9, 115.7 and 142.6 mm Hg.

7. On the basis of the result obtained in solving Problem 6, find the composition of the vapour over the mixture of xylenes at 80 °C.

8. Construct a pressure-composition diagram for the system considered in Example 5 (for the liquid and vapour) and determine the pressure at which an equimolar mixture of dichloroethane and benzene will begin to boil.

What is the composition of the first bubble of vapour?

9. Describe the following processes for the mixtures (Fig. 54) in which the mole fraction of $\text{C}_2\text{H}_5\text{OH}$ is $x=0.1$ and 0.9 ($p=340$ mm Hg):

- (1) single-acting evaporation (simple distillation);
- (2) differential distillation;
- (3) rectification.

8.2. INCOMPLETELY MISCIBLE AND IMMISCIBLE LIQUIDS

The vapour pressures of *incompletely miscible liquids* can be determined approximately with the aid of Eqs. (8.6) and (8.7), considering that the substance which is present in excess is described by the first one of them, and that the vapour pressure (total and partial) over the conjugated solutions, in accordance with *Konovalov's rule*, is the same. The results of the calculations by the equations indicated above will be the more accurate, the lower the mutual solubility of the liquids.

In the limiting case—*immiscible liquids*—the vapour pressure over the system at a given temperature does not depend on the proportion of the liquids and equals the sum of the pressures of the pure compo-

nents. For this reason the boiling point of the mixture will be lower than that of the most volatile component. Distillation with steam is based on this phenomenon.

Examples

1. In accordance with Eq. (8.7), the concentration of a solute that is in two conjugated solutions, on condition of an insignificant mutual solubility, can be approximately calculated: for solution (I) rich in the first component — by the equation

$$(x_2)_I = \frac{p_2}{K_2}$$

and for solution (II) rich in the second component, by the equation

$$(x_1)_{II} = \frac{p_1}{K_1}$$

(1) prove that

$$K_1 = p_1^\circ \frac{(x_1)_I}{(x_1)_{II}} \quad \text{and} \quad K_2 = p_2^\circ \frac{(x_2)_{II}}{(x_2)_I}$$

(2) derive an equation for calculating the composition of an equilibrium mixture, considering that Dalton's law holds for the vapours.

Solution. 1. Since for conjugated solutions, in accordance with Konovalov's rule, the partial pressures of both components are the same, on the basis of Eqs. (8.6) and (8.7) we get

$$p_1 = K_1 (x_1)_{II} = p_1^\circ (x_1)_I \quad \text{or} \quad K_1 = p_1^\circ \frac{(x_1)_I}{(x_1)_{II}} \quad (a)$$

Similarly

$$p_2 = K_2 (x_2)_I = p_2^\circ (x_2)_{II} \quad \text{or} \quad K_2 = p_2^\circ \frac{(x_2)_{II}}{(x_2)_I} \quad (b)$$

2. By Eqs. (8.6) and (8.7) for solutions rich in the first and the second components we get

$$p = p_1 + p_2 = p_1^\circ (x_1)_I + K_2 (x_2)_I = p_1^\circ (x_1)_I + K_2 [1 - (x_1)_I]$$

or

$$(x_1)_I = \frac{p - K_2}{p_1^\circ - K_2}$$

and

$$(x_1^g)_I = \frac{p_1}{p} = \frac{p_1^\circ (x_1)_I}{p_1^\circ (x_1)_I + K_2 [1 - (x_1)_I]} = \frac{p_1^\circ}{p} \frac{p - K_2}{p_1^\circ - K_2} \quad (c)$$

similarly we get

$$p = p_1 + p_2 = p_2^\circ (x_2)_{II} + K_1 (x_1)_{II} = p_2^\circ [1 - (x_1)_{II}] + K_1 (x_1)_{II}$$

or

$$(x_1)_{II} = \frac{p - p_2^\circ}{K_1 - p_2^\circ}$$

and

$$(x_1^g)_{II} = \frac{p_1}{p} = \frac{K_1 (x_1)_{II}}{K_1 (x_1)_{II} + p_2^\circ [1 - (x_1)_{II}]} = \frac{K_1}{p} \frac{p - p_2^\circ}{K_1 - p_2^\circ} \quad (d)$$

2. Find the maximum pressure of vapour at 100°C over a mixture of aniline and water if at this temperature the solubility of water in aniline is 10.3% by weight and of aniline in water is 7.18% by weight, while the vapour pressures of pure aniline and water are 45.7 and 760 mm Hg, respectively. Use the result of solving Example 1 for the calculations.

Solution. We calculate the mole fractions of aniline in conjugated solutions:

in a solution rich in water

$$\frac{7.18/93.12}{7.18/93.12 + 92.82/18.02} = 0.0148$$

and in a solution rich in aniline

$$\frac{89.7/93.12}{89.7/93.12 + 10.3/18.02} = 0.6276$$

By Eqs. (b) and (a) obtained in solving the preceding example, we find

$$K_{C_6H_5NH_2} = 45.7 \times \frac{0.6276}{0.0148} = 1940 \quad \text{and} \quad K_{H_2O} = 760 \times \frac{0.9852}{0.3724} = 2010$$

We calculate the total vapour pressure, assuming that for a solution of aniline in water the vapour pressure of aniline may be computed by Eq. (18.7), and the vapour pressure of water by Eq. (8.6):

$$p = 1940 \times 0.0148 + 760 \times 0.9852 = 28.7 + 748.7 = 777.4 \text{ mm Hg}$$

The vapour pressure over the conjugated solutions which in accordance with Konovalov's rule should also be equal to 777.4 mm Hg, is found to be

$$p = 2010 \times 0.3724 + 45.7 \times 0.6276 = 748.5 + 28.7 = 777.2 \text{ mm Hg}$$

which confirms the correctness of the results of the calculations.

3. Calculate Example 2 graphically by plotting a diagram of the vapour pressure versus the composition of the liquid. Introduce

the following subscripts for the purposes of simplification: H_2O — 1, $\text{C}_6\text{H}_5\text{NH}_2$ — 2, a saturated solution of aniline in water — s-2 and a saturated solution of water in aniline — s-1.

Solution. We lay off along the axes of ordinates $p_1^\circ = 760$ and $p_2^\circ = 45.7$ mm Hg (Fig. 55, points *A* and *B*). After connecting these points respectively to points *e* and *d* and drawing vertical lines corresponding to the concentrations of the saturated solutions, we find the points corresponding to the partial pressures of water and aniline over the conjugated solutions (points *f* and *g*).

Along the lines *Af* and *Bg* the partial pressures of water and aniline diminish up to the limits of mutual solubility of these liquids. In a saturated solution of aniline in water (point *f*) the partial pressure of water equals 750 mm. In a saturated solution of water in aniline (point *g*) the partial pressure of aniline equals about 28 mm Hg. Since the partial pressures of the components over the conjugated solutions are equal, the partial pressure of aniline over its solution in water will equal 28 mm, and the partial pressure of water over its solution in aniline will equal 750 mm. For this reason from points *g* and *f* we draw horizontal lines to their intersection with the vertical ones corresponding to the concentrations of the saturated solutions, and obtain points *i* and *k*. Consequently, the lines *Afie* and *dkgB* show the partial pressures of water and aniline, respectively.

The line *AabB* corresponds to the total pressure. Over a mixture of the saturated solutions it equals $750 + 28 = 778$ mm Hg.

4. On the basis of the data given in the initial conditions of Example 2, plot a diagram of the vapour pressure against the composition (liquid and vapour) for the system aniline ("an")-water ("wat") at 100°C . Use Eqs. (c) and (d) derived in solving Example 1 for the calculations, and the results of solving Example 2.

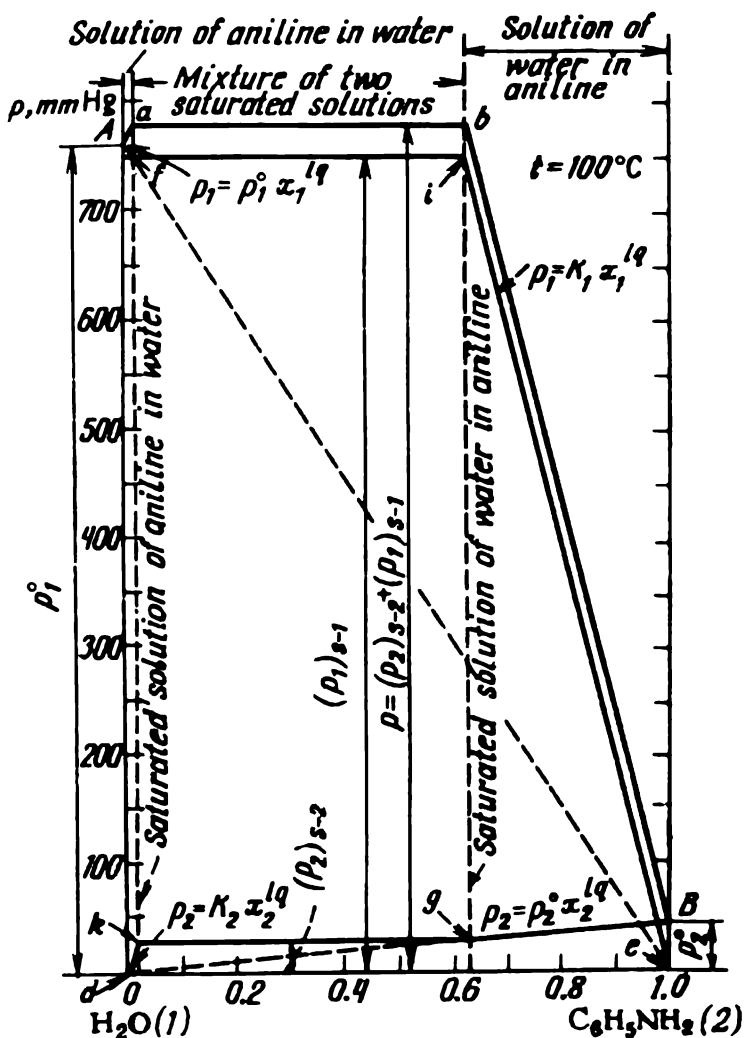


Fig. 55

Solution. In the given case the equations indicated above will become

$$(x_{an}^g)_{II} = \frac{p_{an}^\circ (x_{an})_{II}}{p_{an}^\circ (x_{an})_{II} + K_{wat} [1 - (x_{an})_{II}]}$$
$$(x_{an}^g)_I = \frac{K_{an} (x_{an})_I}{K_{an} (x_{an})_I + p_{wat}^\circ [1 - (x_{an})_I]}$$

We enter the results of the calculations in Table 13.
According to the tabulated data we plot a diagram of p versus x (Fig. 56; for the purposes of clarity section Aac is shown in an increased scale).

Table 13

Solution enriched with water		Solution enriched with aniline	
x_{an}	x_{an}^g	x_{an}	x_{an}^g
0.001	0.002 55	0.627 6	0.0369
0.005	0.0127	0.650	0.0405
0.010	0.0251	0.700	0.050 38
0.0148	0.036 9	0.800	0.08336
		0.900	0.1699
		0.950	0.3017
		0.990	0.6929

5. For cleaning toluene from non-volatile impurities it is distilled with water vapour at $p=745$ mm Hg. At what temperature will distillation proceed? Use the following data for the calculations:

$t, ^\circ\text{C}$	60	70	80	90	100
$p_{\text{H}_2\text{O}}, \text{ kgf/cm}^2$	0.203 1	0.317 7	0.482 9	0.714 9	1.033 2
$p_{\text{C}_6\text{H}_5\text{CH}_3}, \text{ mm Hg}$	139.5	202.4	289.7	404.6	557.2

Solution. After converting $p_{\text{H}_2\text{O}}$ into mm Hg, we plot the lines $p_{\text{H}_2\text{O}}=f(t)$, $p_{\text{C}_6\text{H}_5\text{CH}_3}=f'(t)$ and $p_{\text{tot}}=f''(t)$ (Fig. 57). We find from the plot that at $p=745$ mm Hg the boiling point of the mixture will be about 84°C .

6. Prove that when two immiscible liquids are being distilled and the Mendeleev-Clapeyron equation holds for the vapours, the following equation is observed:

$$\frac{w_2}{w_1} = \frac{p_2^\circ M_2}{p_1^\circ M_1}$$

where w_2 and w_1 are the weight amounts of the components in the vapours. What conclusions follow from this equation?

Solution. Since

$$p_1^\circ V = n_1 RT \text{ and } p_2^\circ V = n_2 RT$$

then

$$\frac{p_1^\circ}{p_2^\circ} = \frac{n_1}{n_2} \text{ or } \frac{p_1^\circ}{p_2^\circ} = \frac{w_1/M_1}{w_2/M_2}$$

It follows from this equation that even if $p_2^\circ \ll p_1^\circ$, then the content of the second component in the distillate may nevertheless be greater

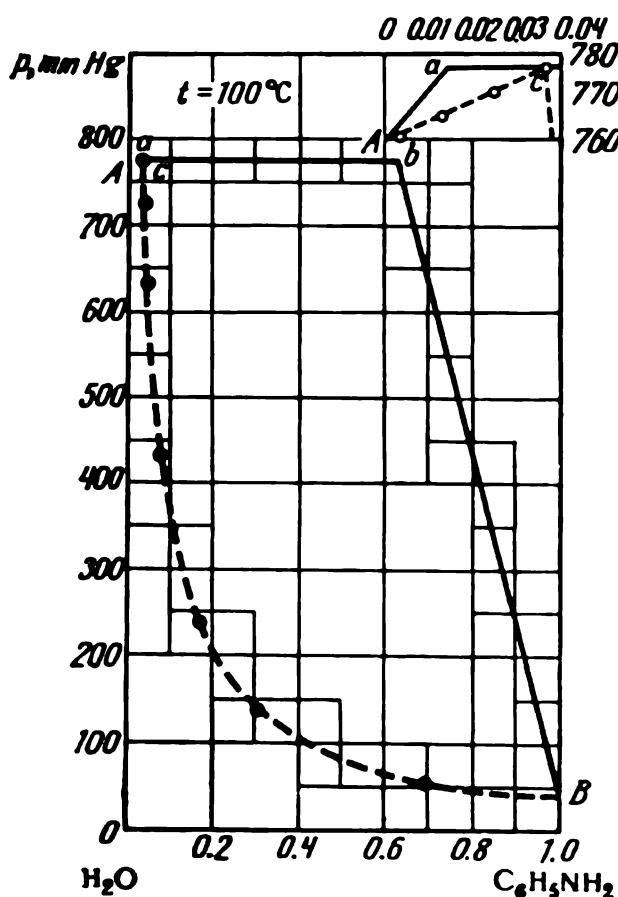


Fig. 56

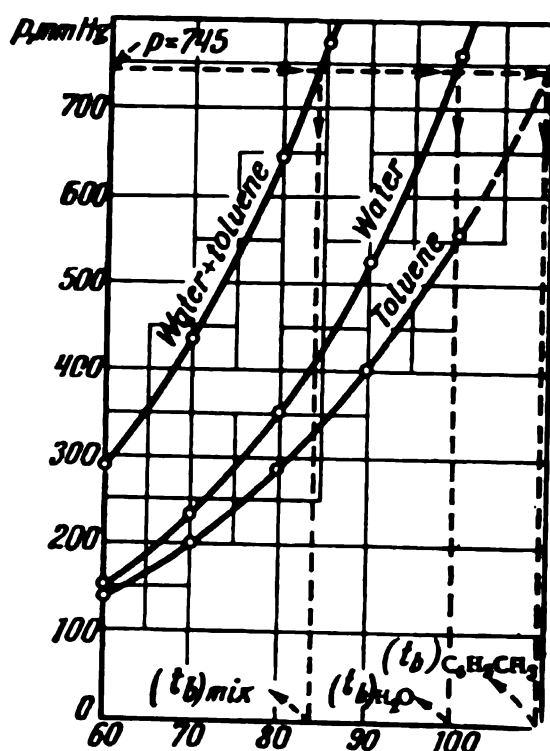


Fig. 57

provided $M_2 \gg M_1$ (hence the expediency of using distillation with water vapour or steam).

7. Determine the consumption of steam for the distillation of 1 kg of toluene at $p=745$ mm Hg. Perform the calculations with the aid of the equation derived in Example 6 according to the data given in Fig. 57.

Solution. From Fig. 57 we find that at $t=84^\circ\text{C}$ the vapour pressure of toluene is about 330, and of water 415 mm Hg. Hence in accordance with the equation indicated above we have

$$\frac{w_{\text{toluene}}}{w_{\text{water}}} = \frac{330 \times 92.13}{415 \times 18.02} = 4.07$$

i.e. about 0.25 kg of steam is used for distilling 1 kg of toluene. The composition of the condensate found (1:4) does not depend on the

composition of the liquid and will be constant as long as both substances are present in the liquid phase, i.e. until all the toluene is distilled off.

8. At $p=745$ mm Hg, toluene is distilled with steam at 84°C (see Example 5).

Find the consumption of steam for the distillation of 100 kg of toluene and the amount of steam condensing in the still if the distillation is conducted in a continuously functioning still into which the toluene is fed at 20°C , while the heat needed for the distillation is received at the expense of cooling of the steam and its partial condensation. The steam is supplied at a gauge pressure of 0.31 kgf/cm² and flows along the tubes with small openings laid in the still. Neglect the losses of heat in the calculations. The heat of vaporization of toluene at 84°C is equal to about 100 kcal/kg, and its heat capacity within the interval of 20 to 84°C may be taken equal to 0.41 kcal/kg \cdot K. The vapour pressures of pure toluene and water at 84°C are respectively 330 and 415 mm Hg (see Fig. 57).

Take the enthalpies of steam needed for the calculations from water property tables.

Solution. The consumption of heat for distillation (ΔH_1) consists of the heat spent on heating the toluene to its boiling point and of the heat of vaporization of the toluene, i.e.

$$\Delta H_1 = 100 (\bar{C}_p)_{\text{tol}} (84 - 20) + 100 (\Delta H_{\text{vap}})_{\text{tol}}$$

where $(\bar{C}_p)_{\text{tol}}$ = mean specific heat capacity of toluene within the interval from 20 to 84°C , kcal/kg \cdot K

$(\Delta H_{\text{vap}})_{\text{tol}}$ = heat of vaporization of toluene, kcal/kg.

Introducing the data given in the initial conditions of the example into this equation, we get

$$\Delta H_1 = 100 \times 0.41 \times 64 + 100 \times 100 = 12\,624 \text{ kcal/kg}$$

The sources of heat are the condensed steam and the uncondensed steam passing over into the receiver of the distillate.

One kilogram of uncondensed steam gives up heat equal to

$$\Delta H'_2 = (H_{\text{wat}}^g)_{379.7} - (H_{\text{wat}}^g)_{357.2} = 641.2 - 632.8 = 8.4 \text{ kcal}$$

One kilogram of condensed steam gives up heat equal to

$$\Delta H''_2 = (H_{\text{wat}}^g)_{379.7} - (H_{\text{wat}}^{\text{liq}})_{357.2} = 641.2 - 84 = 557.2 \text{ kcal}$$

where $(H_{\text{wat}}^g)_{379.7}$ = enthalpy of saturated steam at a pressure of 1.3 atm ($1 + 0.31 \times \frac{735}{760}$)

$(H_{\text{wat}}^g)_{357.2}$ and $(H_{\text{wat}}^{\text{liq}})_{357.2}$ = enthalpies of saturated steam and water at the distillation temperature.

Since the amount of steam spent for distilling 1 kg of toluene is

$$\frac{415 \times 18.02}{330 \times 92.13} = 0.246 \text{ kg}$$

then the amount of water that will pass over into the distillate is

$$100 \times 0.246 = 24.6 \text{ kg}$$

Hence the equation of the heat balance will acquire the form

$$\Delta H = 24.6 [(H_{\text{wat}}^g)_{379.7} - (H_{\text{wat}}^g)_{357.2}] + x [(H_{\text{wat}}^g)_{379.7} - (H_{\text{wat}}^{\text{liq}})_{357.2}]$$

where x is the amount of steam condensing in the still. In accordance with previously found values, we have

$$12\,624 = 24.6 \times 8.4 + 557.2x$$

whence

$$x = \frac{12\,417.4}{557.2} = 22.3 \text{ kg}$$

The total consumption of steam is $24.6 + 22.3 = 46.9 \text{ kg}$.

Problems

1. At 67.8°C the pressure of water vapour is 212 mm Hg, and that of furfural vapour ($\text{C}_4\text{H}_3\text{O} \cdot \text{CHO}$) is 20 mm Hg.

Determine the vapour pressure over a system containing 50% of furfural if its solubility in water at the temperature indicated is 12.1% by weight, and the solubility of water in furfural—about 9.2% by weight.

2. Using the results obtained in solving Problem 1, determine at $t = 67.8^\circ\text{C}$ the vapour pressure over solutions containing (1) 40% by weight of furfural, and (2) 5% by weight of water.

3. Solve Problems 1 and 2 using a diagram of vapour pressure versus composition of the mixture.

4. The boiling points of *m*-xylene at different pressures are expressed by the following data:

p , mm Hg	55.0	110.8	155.5	202.5	305.0
t , $^\circ\text{C}$	62.6	77.7	86.0	93.9	104.9

The pressures of saturated steam are:

t , $^\circ\text{C}$	34.1	41.6	51.6	66.5	83.0	100
p , mm Hg	40	60	100	200	400	760

(1) At what temperature will a mixture of water and *m*-xylene be distilled if a pressure of 400 mm is maintained in the apparatus?

(2) By how many kelvins does the temperature have to be lowered to make distillation possible at half this pressure?

5. According to the results of solving Problem 4, find the content of *m*-xylene (in per cent by weight) in the distillate when it is distilled with steam at $p=400$ mm Hg.

6. Phenol is cleaned of impurities by distillation with superheated steam at 139°C and 750 mm Hg.

(1) What is the consumption of steam in the distillation of 100 kg of phenol if at 139°C the vapour pressure of phenol is 200 mm Hg? Assume that the degree of saturation of the mixture with phenol vapour is 0.7.

(2) By how many times will the consumption of steam diminish if the residual pressure in the system is 200 mm Hg?

7. Determine the consumption of steam in the conditions of the preceding problem if the vapours leave the still cooled to 121.4°C . At this temperature the vapour pressure of phenol is 100 mm Hg.

Explain the result obtained.

Chapter Nine

EQUILIBRIUM CONSTANT AND CHANGE IN STANDARD GIBBS ENERGY

9.1. CALCULATION OF K AND ΔG° ACCORDING TO EQUILIBRIUM DATA

The temperature dependence of the equilibrium constant is expressed by *van't Hoff's equation*:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (9.1)$$

If we consider the standard heat of a reaction ΔH° to be constant ($\Delta C_p=0$), then after the integration we get

$$\log K = -\frac{\Delta H^\circ}{4.576T} + \text{const} = \frac{A}{T} + B \quad (9.2)$$

whence in accordance with the equation

$$\Delta G^\circ = -4.576T \log K \quad (9.3)$$

we get

$$\Delta G^\circ = \Delta H^\circ + \text{const}' T \quad (9.4)$$

When only the values of ΔH_{298}° and ΔG_{298}° are known, the following equation serves for approximate calculations:

$$\log K = 0.000733 (\Delta H_{298}^\circ - \Delta G_{298}^\circ) - \frac{\Delta H_{298}^\circ}{4.576T} \quad (9.5)$$

Approximate calculations can also be performed with the aid of linear equations of $\Delta G^\circ = f(T)$ proposed for certain homologous series, or the calculations can be based on the additivity of ΔG° for various bonds.

For exact calculations within a broad temperature interval, account must be taken of the temperature dependence of ΔH° [see Eq. (2.24), p. 50]. In this case we get

$$\begin{aligned} \log K = & -\frac{\Delta H_0^\circ}{4.576T} + \frac{\Delta a}{1.987} \log T + \frac{\Delta b}{9.150} T + \\ & + \frac{\Delta c}{27.45} T^2 + \frac{\Delta c'}{9.150} T^{-2} + I' \end{aligned} \quad (9.6)$$

or in accordance with Eq. (9.3)

$$\Delta G^\circ = \Delta H_0^\circ - \Delta aT \ln T - \frac{1}{2} \Delta bT^2 - \frac{1}{6} \Delta cT^3 - \frac{1}{2} \Delta c'T^{-1} + IT \quad (9.7)$$

where I' and I are integration constants.

Here, the same as in Eq. (2.24), the quantity Δc relates to substances whose heat capacity is expressed by Eq. (2.8), and $\Delta c'$ to substances whose heat capacity is expressed by Eq. (2.9). For calculations it is necessary to know the temperature dependence of C_p for all the reagents, at least one value of ΔH° (in order to find the value of ΔH_0°)* and one value of K or ΔG° (in order to find the value of I or I'). If the heat capacities of the reagents and a number of values of K at different temperatures are known, the following equation may be used:

$$\begin{aligned} \Sigma = & -4.576 \log K + 2.303 \Delta a \log T + \frac{1}{2} \Delta bT + \\ & + \frac{1}{6} \Delta cT^2 + \frac{1}{2} \Delta c'T^{-2} = \frac{\Delta H_0^\circ}{T} + I \end{aligned} \quad (9.8)$$

which is obtained as a result of transformation of Eq. (9.6) and makes it possible to simultaneously determine ΔH_0° and I from a plot of Σ versus T^{-1} .

If the reaction being studied proceeds in a galvanic cell, then the following equation serves for calculating ΔG° :

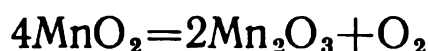
$$\Delta G^\circ = -23\,062zE = \Delta H^\circ - 23\,062zT \left(\frac{\partial E}{\partial T} \right)_p \quad (9.9)$$

which is obtained by combining Eqs. (3.24a) and (3.25a).

The temperature dependences of ΔG° and K can also be determined by combining the equations for the reactions for which the corresponding quantities are known.

Examples

1. In studying the dissociation of manganese dioxide



a pressure of the oxygen of $p_{\text{O}_2} = 569.0$ mm Hg at $T = 836$ K and of $p_{\text{O}_2} = 194.0$ mm Hg at $T = 791$ K was obtained.

* It is simplest to introduce the complex of these quantities into the calculations when the temperature dependence of ΔH° , i. e. Eq. (2.24), is known for a given reaction. In this case, as in others, ΔH° can also be found from the tabulated data by means of the equation

$$\Delta H_T^\circ = \sum [(H_T^\circ - H_0^\circ) + \Delta H_0^\circ]_{\text{pr}} - \sum [(H_T^\circ - H_0^\circ) + \Delta H_0^\circ]_{\text{r}}$$

where ΔH_0° is the hypothetical standard heat of formation for a given reagent at $T = 0$ K, and $(H_T^\circ - H_0^\circ)$ is its standard enthalpy at the temperature T [see Eq. (2.10)].

- (1) Find Eq. (9.2) analytically.
- (2) Determine ΔH° and the value of

$$\Delta C_p = 2(C_p)_{\text{Mn}_2\text{O}_3} + (C_p)_{\text{O}_2} - 4(C_p)_{\text{MnO}_2}$$

within the interval from 298 to 836 K, considering it to be constant if $\Delta H_{298}^\circ = 36\,200$ cal/mol.

- (3) Calculate p_{818} and p_{848} and compare them with the experimentally found values respectively equal to 380.0 and 747.5 mm Hg.

Solution. 1. In the given case

$$K = K_p = p_{\text{O}_2}$$

Therefore in accordance with Eq. (9.2)

$$\log 569.0 = \frac{A}{836} + B \quad \text{and} \quad \log 194.9 = \frac{A}{791} + B$$

The simultaneous solution of the two equations yields $A = -6867$ and $B = 10.969$. Hence

$$\log K_p = \log p_{\text{O}_2} = \frac{-6867}{T} + 10.969$$

2. In accordance with Eq. (9.2) we have

$$\frac{-\Delta H^\circ}{4.576} = -6867$$

whence

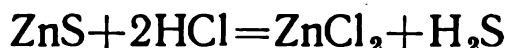
$$\Delta H^\circ = +4.576 \times 6867 = 31\,420 \text{ cal/mol}$$

and

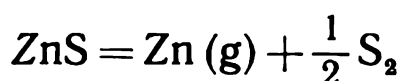
$$\Delta C_p \approx \frac{31\,420 - 36\,200}{836 - 298} = -8.88 \text{ cal/mol} \cdot \text{K}$$

3. According to the derived equation $\log p_{\text{O}_2} = f(T)$, we find $p_{818} = 375.0$ mm and $p_{848} = 749.9$ mm Hg, which differ from the experimentally found values by 1.3 and 0.3%, respectively.

2. On the basis of studying the equilibrium of the reaction



and combining the equilibrium constants obtained with the dissociation constants of zinc chloride, hydrogen chloride and hydrogen sulphide, the constants for the dissociation of zinc sulphide



were found:

$T, \text{ K}$	565	635	1000
$\log K_p$	— 25.287	— 21.310	— 12.526

In another investigation the reduction of zinc sulphide with hydrogen was studied and the following data were obtained:

$T, \text{ K}$	1173	1273	1373
$\log K_p$	−6.552	−5.958	−5.377

(1) Check whether there is an agreement between the data of these investigations.

(2) Calculate K_p at $T=1100 \text{ K}$.

Solution. 1. From the data given in the initial conditions we get

$\frac{1}{T} \times 10^3$	1.770	1.575	1.000	0.852 5	0.785 5	0.728 3
$\log K_p$	−25.287	−21.310	−12.526	−6.552	−5.958	−5.377

Next we plot $\log K_p$ versus $1/T$ (Fig. 58). All the points except one are satisfactorily arranged along a straight line. The point at $T=1000 \text{ K}$

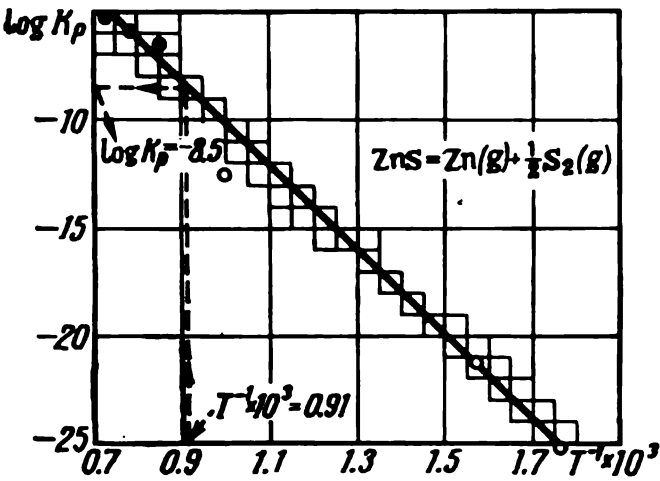


Fig. 58

is an outlier. This is apparently explained by the fact that the vapour pressure of zinc chloride, which becomes considerable at 1000 K, was not taken into account.

2. By interpolation in the chart we find that at $T=1100 \text{ K}$ (i.e. $1/T=0.910 \times 10^{-3}$) we get $\log K_p \approx -8.5$ and $K_p \approx 3.2 \times 10^{-9}$.

3. The following data were obtained in investigating the thermal dissociation of silver sulphide:

$T, \text{ K}$	831	875	880	931	979	981	1033	1107	1136	1196
K_p	0.288	0.271	0.275	0.262	0.259	0.253	0.237	0.228	0.213	0.201

Derive Eq. (9.4) using the method of mean values and assess the accuracy of the equation found.

Solution. We calculate the values of ΔG° by Eq. (9.3):

$T, \text{ K}$. . .	831	875	880	931	979	981	1033	1107	1136	1196
$\Delta G^\circ, \text{ cal/mol}$		2056	2270	2257	2477	2628	2679	2955	3252	3490	3813

Summating the values of ΔG° and T by fives, we compile two equations:

$$\begin{aligned} 11\,688 &= 5A + 4496B \\ 16\,189 &= 5A + 5453B \end{aligned}$$

from which we find $B=4.703$ and $A=-1892$. Consequently

$$\Delta G^\circ = -1892 + 4.703 T$$

The mean error of calculations according to the equation found is 1.6%.

4. As a result of calculating the equilibrium of the reaction



the following values of the equilibrium constant were proposed: $K_p = 0.195$ at $t = 700^\circ\text{C}$ and $K_p = 0.1175$ at $t = 750^\circ\text{C}$.

Find the heat of the reaction and compare it with the most accurate value of $\Delta H_{1000}^\circ = -21\,430$ cal/mol.

Solution. By Eq. (9.2) we have

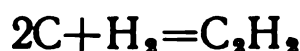
$$\log \frac{0.1175}{0.195} = \frac{\Delta H^\circ}{4.576} \left(\frac{1}{973.2} - \frac{1}{1023.2} \right)$$

whence

$$\begin{aligned} \Delta H^\circ &= \frac{[(-0.929\,96) - (-0.709\,97)] \times 4.576 \times 973.2 \times 1023.2}{50} = \\ &= -20\,050 \text{ cal/mol} \end{aligned}$$

which differs from the most accurate value by 1380 cal, i.e. by 6.4%.

5. For the reaction



we have $\Delta H_{700}^\circ = 53\,787$ cal/mol, and the heat of the reaction changes approximately linearly with the temperature (by about -1.57 cal/K); the quantity $\log (K_p)_{700} = -13.8925$.

1. Use Eq. (9.2) to calculate $\log (K_p)_{1500}$. Assume that when the temperature dependence of the heat is linear, the temperature

$$T = T_1 T_2 \frac{\ln (T_2/T_1)}{T_2 - T_1}$$

corresponds to the value of ΔH° in the indicated equation.

Determine the error of the calculations. The reference value of $\log (K_p)_{1500}$ is -5.0134 .

2. Compare the value obtained in the calculations with that computed directly by Eq. (9.2).

Solution. 1. We calculate the temperature at which the heat of the reaction has to be determined:

$$T = 700 \times 1500 \times 2.303 \frac{\log (1500/700)}{1500 - 700} = 1000 \text{ K}$$

In accordance with the data given in the initial conditions

$$\Delta H_{1000}^\circ = 53\,787 + 300 (-1.57) = 53\,316 \text{ cal/mol}$$

By Eq. (9.2) we have

$$\log (K_p)_{1500} - (-13.8925) = \frac{53\,316}{4.576} \left(\frac{1}{700} - \frac{1}{1500} \right)$$

whence

$$\log (K_p)_{1500} = -13.8925 + 8.8792 = -5.0155$$

which corresponds to an insignificant error in the value of

$$\Delta G_{1500}^{\circ}(-4.576 \times 1500 \times 0.0021 = -14.4 \text{ cal/mol}).$$

2. We find ΔH° by Eq. (9.2):

$$-5.0134 - (-13.8925) = \frac{\Delta H^{\circ}}{4.576} \left(\frac{1}{700} - \frac{1}{1500} \right)$$

whence

$$\Delta H^{\circ} = \frac{8.8791 \times 4.576 \times 700 \times 1500}{800} = 53\,326 \text{ cal/mol}$$

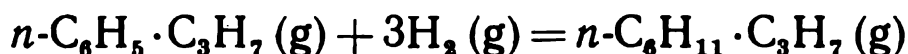
We shall assume that

$$T = \frac{700 + 1500}{2} = 1100 \text{ K}$$

corresponds to this value of ΔH° . Since the exact value of ΔH_{1100}° is 53 151 cal/mol, the difference is 175 cal.

6. The standard heats of formation of gaseous propyl benzene and propyl cyclohexane are respectively 1870 and $-46\,220$ cal/mol, and the standard Gibbs free energies are respectively 32 810 and 11 330 cal/mol.

Find $\log K_p$ for the reaction of hydrogenation



at 287 °C. Compare the result with the experimentally found value equal to -0.955 .

Solution. For the reaction being considered we have

$$\Delta H_{298}^{\circ} = -46\,220 - 1870 = -48\,090 \text{ cal/mol}$$

and

$$\Delta G_{298}^{\circ} = 11\,330 - 32\,810 = -21\,480 \text{ cal/mol}$$

Consequently by Eq. (9.5) we obtain

$$\begin{aligned} \log (K_p)_{500} &= 0.000\,733 [-48\,090 - (-21\,480)] - \frac{48\,090}{4.576 \times 560.2} = \\ &= -19.505 + 18.760 = -0.745 \end{aligned}$$

A satisfactory coincidence with the experimentally found value is due to a comparatively small temperature difference ($\Delta T = 262$ K).

7. Find Eq. (9.4) and calculate ΔG_{900}° for equilibrium of the reaction



if the values of the Gibbs energies of the C=C and C—C bonds are:

$T, \text{ K}$	298	500	700
$\Delta G_{\text{C}=\text{C}}^{\circ}, \text{ kcal/mol}$	22.6	21.2	19.6
$\Delta G_{\text{C}-\text{C}}^{\circ}, \text{ kcal/mol}$	6.4	9.2	11.9

Solution. For the given reaction

$$\Delta G^\circ = \Delta G_{C-C}^\circ - 2\Delta G_{C-C}^\circ$$

Hence

$$\Delta G_{298}^\circ = 9.8; \quad \Delta G_{500}^\circ = 2.8; \quad \text{and} \quad \Delta G_{700}^\circ = -4.2 \text{ kcal/mol}$$

Since the value of ΔG° changes by 3500 cal/mol for every 100 kelvins of the change in temperature, then

$$\Delta G^\circ = 20\,300 - 35T \quad \text{and} \quad \Delta G_{900}^\circ = -11\,200 \text{ cal/mol}$$

8. In studying the reaction of hydrogenation of ethylene



the following results were obtained:

$t, ^\circ\text{C}$	400	450	500	600	650	700
$\log K_p$	3.824	3.119	2.500	1.500	1.076	0.708

The standard heats of formation of C_2H_4 and C_2H_6 are respectively equal to 12 426 and $-20\,236$ cal/mol.

Find Eq. (9.7) and calculate ΔG_{298}° if

$$\begin{aligned} (C_p)_{H_2} &= 6.744 + 0.2774 \times 10^{-3} T + 0.1956 \times 10^{-6} T^2 \\ (C_p)_{C_2H_4} &= 2.08 + 31.1 \times 10^{-3} T - 10.66 \times 10^{-6} T^2 \\ (C_p)_{C_2H_6} &= 1.62 + 42.1 \times 10^{-3} T - 13.9 \times 10^{-6} T^2 \end{aligned}$$

Compare the results of the solution with the most accurate data on the standard Gibbs free energies of ethane (-7860 cal/mol) and ethylene (16 282 cal/mol).

Solution. We compute the coefficients Δa , Δb , Δc and ΔH_{298}° :

$$\begin{aligned} \Delta a &= 1.62 - (2.08 + 6.744) = -7.204 \\ \Delta b &= [42.1 - (31.1 + 0.2774)] \times 10^{-3} = 10.723 \times 10^{-3} \\ \Delta c &= \{-13.9 - [(-10.66) + 0.1956]\} \times 10^{-6} = \\ &= -3.4356 \times 10^{-6} \\ \Delta H_{298}^\circ &= -20\,236 - 12\,496 = -32\,732 \text{ cal/mol} \end{aligned}$$

We determine ΔH_0° . In accordance with Eq. (2.24) we have

$$\begin{aligned} -32\,732 &= \Delta H_0^\circ - 7.204 \times 298.2 + 5.3615 \times 10^{-3} \times \\ &\quad \times 298.2^2 - 1.1452 \times 10^{-6} \times 298.2^3 \end{aligned}$$

whence

$$\Delta H_0^\circ = -32\,732 + 2148 - 477 + 30 = -31\,031 \text{ cal/mol}$$

Equation (9.7) becomes

$$\begin{aligned} \Delta G^\circ &= -31\,031 + 16.59T \log T - 5.3615 \times 10^{-3} T^2 + \\ &\quad + 0.5726 \times 10^{-6} T^3 + IT \end{aligned}$$

To determine I we calculate the values of ΔG° for all the temperatures by Eq. (9.3):

T, K	673.2	723.2	773.2	873.2	923.2	973.2
$\Delta G^\circ, \text{cal/mol}$	-11 780	-10 320	-8843	-5992	-4545	-3152

By the equation $\Delta G^\circ = f(T)$ we find

T, K	673.2	723.2	773.2	873.2	923.2	973.2
I	-14.97	-15.22	-15.39	-15.39	-16.04	-16.25

Mean value of $I = -15.62$

Consequently,

$$\Delta G^\circ = -31\,031 + 16.59T \log T - 5.3615 \times 10^{-3} T^2 + 0.5726 \times 10^{-6} T^3 - 15.62T$$

and

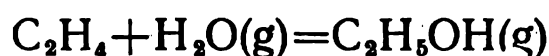
$$\Delta G_{298}^\circ = -31\,031 + 12\,242 - 477 + 15 - 4658 = -23\,909 \text{ cal/mol}$$

According to tabulated data

$$\Delta G_{298}^\circ = -7860 - 16\,282 = -24\,142 \text{ cal/mol}$$

which differs from the calculated value by 233 cal, or 1%.

9. The temperature dependence of the equilibrium constant for the reaction of hydration of ethylene



is expressed by the following data, taken from five sources:

T, K	653	418	448	473	498	523	448	473	498
$-\log K$	2.971	1.168	1.444	1.783	1.971	2.174	1.533	1.765	2.007
T, K	523	548	423	593	623	651			
$-\log K$	2.202	2.417	1.310	2.728	2.827	2.900			

(1) Find Eq. (9.7) if

$$\begin{aligned} (C_p)_{\text{C}_2\text{H}_5\text{OH}}^\text{g} &= 2.16 + 49.7 \times 10^{-3} T - 15.53 \times 10^{-6} T^2 \\ (C_p)_{\text{C}_2\text{H}_4}^\text{g} &= 2.08 + 31.1 \times 10^{-3} T - 10.66 \times 10^{-6} T^2 \\ (C_p)_{\text{H}_2\text{O}}^\text{g} &= 7.55 + 1.3523 \times 10^{-3} T + 0.8658 \times 10^{-6} T^2 \end{aligned}$$

Use Eq. (9.8) for the calculations.

(2) Find ΔH_{298}° .

Solution. 1. According to the data given in the initial conditions we compute

$$\Delta a = 2.16 - (2.08 + 7.55) = -7.47$$

$$\Delta b = [49.7 - (31.1 + 1.3523)] \times 10^{-3} = 17.2477 \times 10^{-3}$$

$$\Delta c = \{-15.53 - [(-10.66) + 0.8658]\} \times 10^{-6} = -5.7358 \times 10^{-6}$$

Hence Eq. (9.8) becomes

$$\Sigma = -4.576 \log K + 2.303 (-7.47) \log T + \frac{1}{2} \times 17.2477 \times 10^{-3} T + \frac{1}{6} (-5.7358) \times 10^{-6} T^2 = \frac{\Delta H_0^\circ}{T} + 1$$

or

$$-4.576 \log K - 17.203 \log T + 8.6238 \times 10^{-3} \cdot T - 0.95597 \times 10^{-6} \times T^2 = \frac{\Delta H_0^\circ}{T} + 1$$

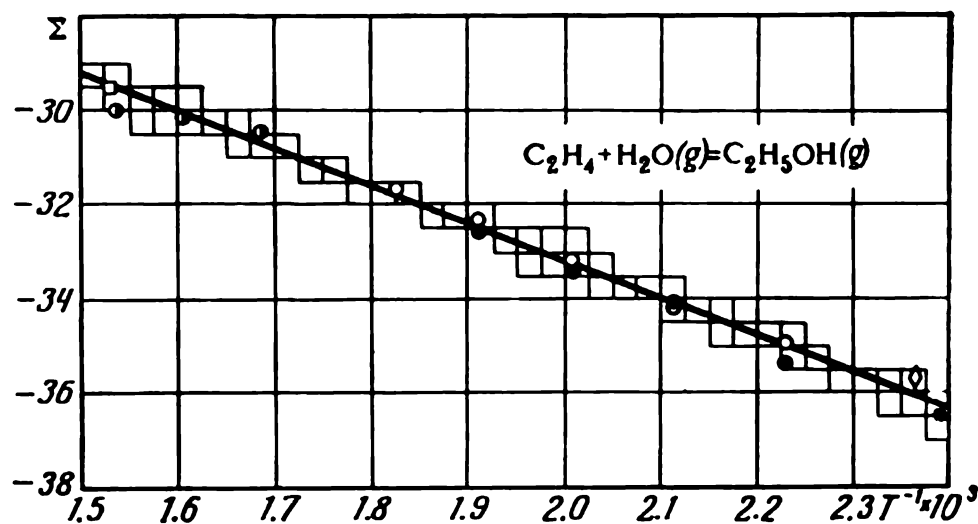


Fig. 59

According to the last equation we get

$1/T$	0.001 531	0.002 392	0.002 232	0.002 114	0.002 008
Σ	-29.61	-36.31	-35.33	-33.99	-33.34
$1/T$	0.001 912	0.002 232	0.002 114	0.002 008	0.001 912
Σ	-32.57	-34.92	-34.07	-33.16	-32.44
$1/T$	0.001 825	0.002 364	0.001 686	0.001 605	0.001 536
Σ	-31.62	-35.71	-30.45	-30.14	-29.92

On the basis of these data we plot Σ against T^{-1} (Fig. 59) and use the chart to find

$$\Delta H_0^\circ = \frac{5.9 \cdot 10^3}{0.75} = -7870 \quad \text{and} \quad I = -17.5$$

Therefore

$$\Delta G^\circ = -7870 + 7.47T \ln T - 8.6238 \times 10^{-3} T^2 + 0.956 \times 10^{-6} T^3 - 17.5T$$

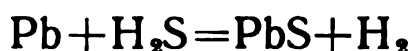
2. We calculate ΔH_{298}° . Since

$$\Delta H^\circ = -7870 - 7.47T + 8.6238 \times 10^{-3} T^2 - 1.912 \times 10^{-6} T^3$$

then

$$\Delta H_{298}^{\circ} = -7870 - 7.47 \times 298.2 + 8.6238 \times 10^{-3} \times 298.2^2 - 1.912 \times 10^{-6} \times 298.2^3 = -9.382 \text{ cal/mol}$$

10. It was established that for an electrochemical cell in which the reaction



proceeds, the temperature dependence of the e.m.f. is expressed by the equation

$$E = 0.28501 - 0.3325 \times 10^{-3} (t - 25) + 6.15 \times 10^{-6} (t - 25)^2$$

For the reaction of reduction of PbS with hydrogen, the following data were obtained:

$t, ^\circ\text{C}$	806	896	998
$1/K$	0.039	0.082	0.176

(1) Find the dependence of ΔG° on T and ΔG_{298}° .

(2) Do the experimental data given above agree with each other? Use the data of Example 5 in Sec. 2.5 (p. 53) for the calculations.

Solution. 1. In accordance with Eq. (9.8) and the data found in solving the example indicated above we have

$$I = -4.576 \log K + 2.303 \times 3.48 \log T + 0.775 \times 10^{-3} T + \frac{19990}{T}$$

For $T=1079$ K ($t=806^\circ\text{C}$) we have

$$I = -4.576 \log \frac{1}{0.039} + 8.014 \log 1079 + 0.775 \times 10^{-3} \times 1079 + \frac{19990}{1079} = -6.446 + 24.307 + 0.8362 + 18.526 = 37.22$$

For $T=1169$ K ($t=896^\circ\text{C}$) we have

$$I = -4.576 \log \frac{1}{0.082} + 8.014 \log 1169 + 0.775 \times 10^{-3} \times 1169 + \frac{19990}{1169} = 37.62$$

For $T=1271$ K ($t=998^\circ\text{C}$) we have

$$I = -4.576 \log \frac{1}{0.176} + 8.014 \log 1271 + 0.775 \times 10^{-3} \times 1271 + \frac{19990}{1271} = 38.14$$

The mean value is $I=37.66$. Consequently

$$\Delta G^\circ = -19990 - 8.014T \log T - 0.775 \times 10^{-3} T^2 + 37.66T$$

2. We calculate ΔG_{298}° for the reaction of H_2S with crystalline lead. For this purpose we use the equation found to determine $\Delta G_{600.5}^\circ$ (since at $T=600.5$ K crystalline lead is in equilibrium with liquid lead);

$$\Delta G_{600.5}^\circ = -19\,990 - 8.014 \times 600.5 \times 2.778\,51 - 0.775 \times 10^{-3} \times 600.5^2 + 37.66 \times 600.5 = -11\,030 \text{ cal/mol}$$

Using the value of $\Delta H^\circ = f(T)$ for the reaction of hydrogen sulphide with solid lead (see the solution of Example 5 in Sec. 2.5):

$$\Delta H^\circ = -19\,040 + 4.56T - 0.265 \times 10^{-3}T^2$$

we get for this reaction

$$\Delta G^\circ = -19\,040 - 10.502T \log T + 0.265 \times 10^{-3}T^2 + I'T$$

We find the integration constant I' by substituting $\Delta G_{600.5}^\circ = -11\,030$ cal/mol:

$$-11\,030 = -19\,040 - 10.502 \times 600.5 + 0.265 \times 10^{-3} \times 600.5^2 + 600.5I'$$

whence $I' = 23.68$. Hence

$$\Delta G^\circ = -19\,040 - 10.502T \log T + 0.265 \times 10^{-3}T^2 + 23.68T$$

and

$$\Delta G_{298}^\circ = -19\,040 - 10.502 \times 298.2 \times 2.47451 + 0.265 \times 10^{-3} \times 298.2^2 + 23.68 \times 298.2 = -15\,090 \text{ cal/mol}$$

By Eq. (9.9) we find

$$\Delta G_{298}^\circ = -23.066 \times 2 \times 0.285\,01 = -13\,150 \text{ cal/mol}$$

The result of the calculations shows that the data of both investigations coincide with sufficient accuracy.

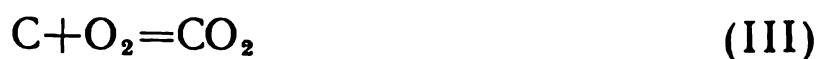
11. Find the equilibrium constant for the reaction



at $T=400, 800$ and 1200 K if ΔG° for the reactions



and



has the following values:

$T, \text{ K}$	400	800	1200
$\Delta G_{\text{II}}^\circ, \text{ cal/mol}$	-35 007	-43 677	-52 153
$\Delta G_{\text{III}}^\circ, \text{ cal/mol}$	-94 325	-94 539	-94 661

Solution. Since $(I) = 2(II) - (III)$, then

$$\Delta G_I^\circ = 2\Delta G_{II}^\circ - \Delta G_{III}^\circ \text{ and } (K_p)_I = \frac{(K_p)_{II}^2}{(K_p)_{III}}$$

The results of the calculations are given below:

T, K	400	800	1200
$\Delta G_I^\circ, \text{ cal/mol}$	+24.311	+7185	-9645
$(K_p)_I$	5.192×10^{-14}	1.088×10^{-2}	57.13

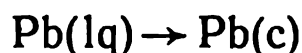
12. The following equations were proposed for calculating ΔG° for the reactions of formation of lead chloride from solid lead:

$$\Delta G^\circ = 85\,204 - 8.283T \ln T + 3.612 \times 10^{-3}T^2 - 2.98 \times 10^{-6}T^3 + 24.01T$$

and from liquid lead:

$$\Delta G^\circ = 83\,072 - 9.353T \ln T + 1.412 \times 10^{-3}T^2 + 5.85 \times 10^{-6}T^3 + 51.2T$$

Find the equation $\log K = f(T)$ for the process



Solution. Subtracting the first equation from the second one, we get

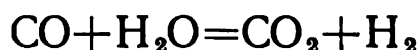
$$\Delta G^\circ = -2132 - 1.070T \ln T - 2.200 \times 10^{-3}T^2 + 8.83 \times 10^{-6}T^3 + 27.19T$$

or in accordance with Eq. (9.3)

$$\log K = \frac{466}{T} - 0.539 \log T - 0.481 \times 10^{-3}T + 1.93 \times 10^{-6}T^2 + 5.943$$

Problems

1. Find an approximate value of the heat of the reaction



if it is known that the equilibrium constant of this reaction at $T = 1100$ K diminishes by about 0.32% per kelvin. Appraise the accuracy of the calculations if at $T = 1100$ K the heats of formation of carbon monoxide, steam and carbon dioxide are respectively -26 909, -59 384 and -94 634 cal/mol.

2. In studying the equilibrium of dehydrogenation of ethyl alcohol

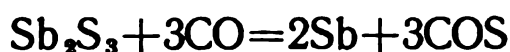


within the temperature interval from 181 to 202 °C the following approximate equation was proposed:

$$\log K_p = -\frac{2100}{T} + 4.66$$

Find the standard heat of formation of the ester if the standard heat of formation of the alcohol is $-56\,510$ cal/mol.

3. In investigating the equilibrium of the reaction



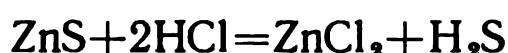
the following data were obtained:

$T, \text{ K}$	1093	1195	1297
K_p	0.012 05	0.0150	0.0208

(1) find Eq. (9.2) graphically:

(2) find the temperature at which $K_p = 0.03$.

4. In studying the equilibrium of the reaction



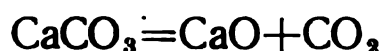
the following values of the equilibrium constant were obtained:

$t, ^\circ\text{C}$	294	362
K_p	1.14	1.67

Determine ΔH° graphically within the cited temperature interval.

5. The dissociation pressure of calcium carbonate is 626 mm Hg at $t_1 = 892^\circ\text{C}$ and 775 mm Hg at $t_2 = 910^\circ\text{C}$.

Determine the heat of the reaction



and compare it [at $t = (t_1 + t_2)/2$] with the result of the calculations by the equation found in solving Problem 7 of Sec. 2.5 (p. 56).

What does the result of this comparison indicate?

6. As a result of investigating the dissociation of various sulphides it was proposed to calculate the dissociation pressure for the reaction



by the equation

$$\log p_{\text{S}_2} = -\frac{14\,330}{T} + 5.8$$

and for the reaction



by the equation

$$\log p_{\text{S}_2} = -\frac{15\,430}{T} + 8.1$$

What amount of stannous sulphide would it be necessary to obtain from tin and sulphur to decompose 1 kg of ferrous sulphide? Assume that the heat losses equal 30%.

7. In investigating the reaction of hydrogenation of toluene



it was established that $(K_p)_{555} = 0.646$.

Calculate $\log(K_p)_{505.8}$ and compare it with the experimentally found value equal to 1.312. The standard heats of formation of gaseous toluene and methyl cyclohexane are respectively 11 950 and $-36\,990$ cal/mol.

8. For the reaction of isomerization



we have $\Delta H_{298}^\circ = -1640$ cal/mol and $\Delta G_{298}^\circ = -542$ cal/mol.

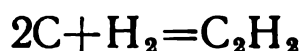
Calculate K_p at $t = 150^\circ\text{C}$ and compare the result with the value 1.7 found from experimental data.

9. To calculate ΔG° for the formation of acetylene hydrocarbons, the following approximate linear equation (9.4) was proposed:

$$\Delta G^\circ = 70\,425 - 8633N + 26.09NT - 67.5T$$

where N is the number of carbon atoms.

Find $\log(K_p)_{1000}$ for the reaction



Compare the result with the value -8.993 cal/mol.

10. Calculate ΔG_{1000}° for the reaction

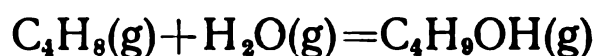


and compare it with the most accurate value equal to 28 249 cal/mol. Use the following values of ΔG° for the bonds $\text{C}=\text{C}$ and $\text{C}-\text{H}$:

$$\Delta G_{\text{C}=\text{C}}^\circ = 28\,024 + 2.75T \ln T - 1.4 \times 10^{-3}T^2 - 0.80 \times 10^{-6}T^3 - 24.86T$$

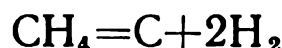
$$\Delta G_{\text{C}-\text{H}}^\circ = -3344.5 + 2.97T \ln T - 2.25 \times 10^{-3}T^2 + 0.188 \times 10^{-6}T^3 - 13.68T$$

11. Determine $(K_p)_{500}$ for the reaction



if at $T = 500$ K the value of $(\Delta G_{\text{form}}^\circ)_{\text{H}_2\text{O}} \approx -52.3$ kcal/mol, and $\Delta G_{\text{C}-\text{C}}^\circ = 9.2$, $\Delta G_{\text{C}=\text{C}}^\circ = 21.2$, $\Delta G_{\text{C}-\text{H}}^\circ = -1.2$ and $\Delta G_{\text{C}-\text{OH}}^\circ = 30.1$ kcal/mol.

12. Find Eq. (9.6) for the reaction



if $\log(K_p)_{1000} = 0.988$, $\Delta H_{500}^\circ = 19\,302$ cal/mol and

$$(C_p)_{\text{C}} = -2.01 + 134.9 \times 10^{-3}T - 6.39 \times 10^{-6}T^2$$

$$(C_p)_{\text{H}_2} = 6.744 + 2.774 \times 10^{-3}T + 0.1956 \times 10^{-6}T^2$$

$$(C_p)_{\text{CH}_4} = 4.4 + 154.245 \times 10^{-3}T - 2.686 \times 10^{-6}T^2$$

Use the found equation to calculate $\log(K_p)_{500}$ and compare the result with the values -3.31 to -3.50 .

13. For the reaction of hydrogenation of benzene to cyclohexane



at $p=1$ atm and within the interval of 223 to 276 °C the following equation was proposed:

$$\log K_p = \frac{9590}{T} - 9.9194 \log T + 0.002285T + 8.565$$

Find the equation of $\Delta H^\circ = f(T)$ and calculate ΔH_{298}° . Compare the results obtained in calculating the standard heat of the reaction according to the equilibrium data and to the heats of formation. The standard heats of formation of gaseous benzene and cyclohexane are respectively 19 820 and -29 430 cal/mol.

14. For the reaction



we have $(K_p)_{1300} = 1.94$ and $\Delta H_{298}^\circ = 78\,385$ cal/mol. Calculate $(K_p)_{1500}$ if the enthalpies of the reagents are:

Substance	Na_2CO_3	C	H_2O	NaOH	CO
$H_{298}^\circ - H_0^\circ$, cal/mol	4603	166	2812	2534	3942
$H_{1400}^\circ - H_0^\circ$, cal/mol	55 579	5074	23 379	25 400	12 357

15. Below are given the values of the equilibrium constants for the reaction of hydrogenation of benzene



within the interval from 230 to 280 °C:

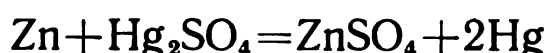
T , K	503	523	530	534	541	548	553
$\log K_p$	2.013	1.101	0.865	0.757	0.550	0.218	0.210

Using Eq. (9.8), derive Eqs. (9.6) and (9.7) and compute ΔH_{298}° if

$$\begin{aligned}(C_p)_{\text{C}_6\text{H}_6}^\circ &= -5.04 + 95.63 \times 10^{-3}T - 40.60 \times 10^{-6}T^2 \\ (C_p)_{\text{H}_2}^\circ &= 6.774 + 0.2774 \times 10^{-3}T + 0.1956 \times 10^{-6}T^2 \\ (C_p)_{\text{C}_6\text{H}_{12}}^\circ &= -7.701 + 125.675 \times 10^{-3}T - 41.584 \times 10^{-6}T^2\end{aligned}$$

The most accurate value of $\Delta H_{298}^\circ = -49\,250$ cal/mol.

16. The temperature dependence of the e.m.f. for a cell in which the reaction

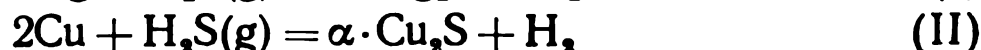


proceeds is expressed by the following equation:

$$E = 1.4328 - 0.00119(t-15) - 0.0000057(t-15)^2$$

Determine the heat of the reaction during operation of the cell if $t=25$ °C.

17. For the reactions



proceeding in a galvanic cell we have

$$E = 0.03615 - 0.0815 \times 10^{-3} (t - 25) + 0.05 \times 10^{-6} (t - 25)^2 \quad (\text{I})$$

$$E = 0.24666 - 0.1695 \times 10^{-3} (t - 25) - 0.25 \times 10^{-6} (t - 25)^2 \quad (\text{II})$$

Determine ΔH_{298}° for the reactions



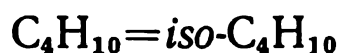
and



if the standard heat of formation of hydrogen sulphide is -4800 cal/mol.

Compare the results of the calculations with the values found using a thermochemical procedure: $(\Delta H_{298}^\circ)_{\text{III}} = -7560 \pm 360$ cal/mol and $(\Delta H_{298}^\circ)_{\text{IV}} = -19300 \pm 500$ cal/mol.

18. How will the temperature affect the equilibrium of the reaction



if the changes in the standard Gibbs energy are equal to $(\Delta G_{\text{C}_4\text{H}_{10}}^\circ)_{800} = 44550$, $(\Delta G_{\text{C}_4\text{H}_{10}}^\circ)_{1000} = 64710$, $(\Delta G_{\text{iso-C}_4\text{H}_{10}}^\circ)_{800} = 45820$ and $(\Delta G_{\text{iso-C}_4\text{H}_{10}}^\circ)_{1000} = 66790$ cal/mol.

Determine the approximate value of ΔH_{900}° and compare it with the accurate value if at 900 K the heats of formation of butane and isobutane are, respectively, -36540 and -38100 cal/mol.

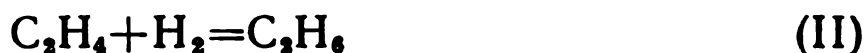
19. For calculating the equilibrium constant of the reaction



the equation

$$\log K_p = -\frac{2413}{T} - 5.589 \log T + 1.025 \times 10^{-3} T + 0.175 \times 10^{-6} \times T^2 + 13.04$$

has been proposed, and for the reaction



the equation

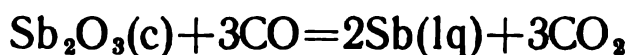
$$\log K_p = \frac{6366}{T} - 2.961 \log T + 0.7668 \times 10^{-3} T - 0.1764 \times 10^{-6} \times T^2 + 2.344$$

Find the equation of $\log K_p = f(T)$ for the reaction



and compute ΔG_{1000}° .

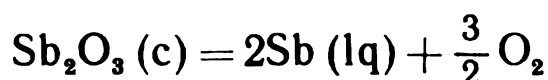
20. To calculate equilibrium of the reaction



the following equation was proposed:

$$\Delta G^\circ = -33\,461 + 34.286 T \log T - 11.1 \times 10^{-3} T^2 + \\ + 0.96 \times 10^{-6} T^3 - 88.65 T$$

For the reactions of formation of carbon monoxide and dioxide from elements we have $(\Delta G_{700}^\circ)_{\text{CO}} = -41\,526$, $(\Delta G_{1000}^\circ)_{\text{CO}} = -47\,942$, $(\Delta G_{700}^\circ)_{\text{CO}_2} = -94\,497$ and $(\Delta G_{1000}^\circ)_{\text{CO}_2} = -94\,610$ cal/mol. Find ΔG_{700}° and ΔG_{1000}° for the reaction



9.2. CALCULATION OF K AND ΔG° ACCORDING TO THERMAL DATA

For reactions in *condensed* systems, Eq. (9.7) becomes

$$\Delta G^\circ = \Delta H_0^\circ - \frac{1}{2} \Delta b^\circ T^2 - \frac{1}{6} \Delta c^\circ T^3 \quad (9.10)$$

or

$$\Delta G^\circ = \Delta H_0^\circ - T \int_0^T \frac{dT}{T^2} \int_0^T \Delta C_p^\circ dT \quad (9.11)$$

The values of $\int_0^T dT/T^2 \int_0^T C_p^\circ dT$ for many substances at different temperatures can be found in reference tables.

For *homogeneous and gaseous heterogeneous* reactions, the *Nernst equations* are used, namely, the accurate one

$$\log K_p = -\frac{\Delta H_0^\circ}{4.576T} + \frac{(\Delta C_p)_{\text{const}}}{1.987} \log T + \\ + \frac{1}{4.576} \int_0^T \frac{dT}{T^2} \int_0^T (\Delta C_p)_{f(T)} dT + \Delta j \quad (9.12)$$

where $(C_p)_{\text{const}}$ = addend of C_p independent of the temperature (for crystalline bodies it equals zero)

$(C_p)_{f(T)}$ = temperature function of the heat capacity (the term containing these quantities can be found with the aid of tables of Einstein's functions (Appendix 3))

j = true chemical constant for each reagent (for crystalline bodies it equals zero).

and the approximate ones

$$\log K_p = -\frac{\Delta H_0^\circ}{4.576T} + 1.75\Delta n \log T + \frac{\Delta b}{9.15} T + \Delta i \quad (9.13)$$

$$\log K_p = -\frac{\Delta H_{298}^\circ}{4.576T} + 1.75\Delta n \log T + \Delta i \quad (9.14)$$

Equations (9.13) and (9.14) contain the conditional chemical constants i . The former equation is based on the assumption that

$$\Delta C_p = 3.5\Delta n + \Delta bT$$

where Δn is the change in the number of moles during a reaction, and the latter equation assumes that $\Delta H_0^\circ = \Delta H_{298}^\circ$ and that $\Delta C_p = \text{const.}$

The standard entropies of substances needed to calculate equilibrium can be found in the following ways.

1. On the basis of the temperature dependence of the heat capacity and the values of the heats of phase transitions according to the equation

$$S_T = \sum \int \frac{C_p dT}{T} + \sum \frac{\Delta H_{\text{ph. tr}}}{T} \quad (9.15)$$

the integrals being taken graphically, while the part of the first integral covering the temperature interval from 0 K to the temperature below which no data are available on the dependence of C_p on T is found by interpolation or by special procedures. The value obtained for gaseous substances is reduced to the standard state with the aid of Eqs. (3.10) and (4.2). If the standard entropy S_{298}° is known, then the value of S_T° can be found according to the dependence of C_p on T or H on T .

2. On the basis of spectroscopic data (for substances in the state of an ideal gas at $p=1$ atm) by the equation

$$S_T^\circ = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T + R \ln \sum g_i e^{-\epsilon_i/kT} + \frac{R}{kT} \times \\ \times \frac{\sum \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} - 2.313 \quad (9.16)$$

3. According to molecular constants (for substances in the state of an ideal gas at $p=1$ atm):

for linear molecules according to the equation

$$S_T^\circ = \frac{3}{2} R \ln M + \frac{7}{2} R \ln T + R \ln I - R \ln \sigma + \\ + R \sum_1^m \left[\frac{\Theta/T}{e^{\Theta/T} - 1} - \ln \left(1 - e^{-\frac{\Theta}{T}} \right) \right] + 175.353 \quad (9.17)$$

and for non-linear ones according to the equation

$$S_T^\circ = \frac{3}{2} R \ln M + 4R \ln T + \frac{1}{2} R \ln (I_A \cdot I_B \cdot I_C) - R \ln \sigma + \\ + R \sum_1^m \left[\frac{\Theta/T}{e^{\Theta/T} - 1} - \ln \left(1 - e^{-\frac{\Theta}{T}} \right) \right] + 265.329 \quad (9.18)$$

where I_A , I_B and I_C = principal moments of inertia

σ = symmetry number

$m = 3n - 5$ for linear molecules and $3n - 6$ for non-linear ones (n is the number of atoms in a molecule).

The terms containing $\Sigma f(\Theta/T)$ can be determined directly from the tables of Einstein's functions in which the values of the corresponding quantities per degree of freedom are given (Appendix 3).

4. According to the known value of ΔS° for a reaction including the substance being studied, and according to the entropies of all the other substances (for example, according to the temperature coefficient of the e. m. f.).

5. From data on the residual rays.

6. According to various empirical methods.

Having determined ΔS_T° for a reaction in one way or another and having at our disposal the value of ΔH_T° , we can calculate ΔG° by Eq. (3.22a):

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (9.19)$$

The latter is used to compute the integration constants of the equations $\log K = f(T)$ and $\Delta G^\circ = f'(T)$.

The calculations can also be performed with the aid of the relationship obtained by combining Eqs. (9.19) and (9.9).

If the standard entropies S_{298}° and reaction heats ΔH_{298}° are used for the calculations, the change in the standard Gibbs energy at higher temperatures can be determined by the equation

$$\Delta G^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - T \int_{298}^T \frac{\Delta C_p}{T} dT + \\ + \int_{298}^T \Delta C_p dT = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - T \int_{298}^T \frac{dT}{T^2} \times \int_{298}^T \Delta C_p dT \quad (9.20)$$

the last term of whose right-hand part is calculated from a relationship $\Delta C_p = f(T)$. If it is expressed by a power series [Eq. (2.23)], then the *method of Temkin and Shwartsman* is expedient for simpli-

fying the calculations, introducing the designations

$$M_0 = \ln \frac{T}{298.2} - 1 + \frac{298.2}{T}$$
$$M_n = \frac{T^n}{n(n+1)} + \frac{298.2^{n+1}}{(n+1)T} - \frac{298.2^n}{n}$$

where $n=1, 2$ and -2 . Equation (9.20) can be obtained, using this method, in the form

$$\Delta G^\circ = \Delta H^\circ_{298} - T\Delta S^\circ_{298} - (M_0 \Delta a + M_1 \Delta b + M_2 \Delta c + M_{-2} \Delta c') T \tag{9.21}$$

The values of the coefficients M_0, M_1, M_2 and M_{-2} are given in Appendix 10.

It should be indicated in conclusion that when the values of $(G^\circ - H^\circ_0)/T$ (they are found on the basis of spectroscopic data) and ΔH°_0 are known for all the reagents, the following formula should be used for the calculations:

$$\log K_p = -\frac{1}{4.576} \left[\Delta \left(\frac{G^\circ - H^\circ_0}{T} \right) + \frac{\Delta H^\circ_0}{T} \right] \tag{9.22}$$

The values of ΔH°_0 and $(G^\circ - H^\circ_0)/T$ for a number of selected substances are given in Appendix 11.

Examples

1. On the basis of the data given in Table 14, calculate ΔG°_{298} and plot the temperature dependences of ΔH° and ΔG° for the reaction



if $\Delta H^\circ_{298} = -26\,700$ cal/mol.

Table 14

T	Si		C (graphite)		$\frac{1}{2}$ SiC	
	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$
50	6.10	2.06	1.85	0.61	0.66	0.22
100	60.0	26.1	14.5	6.94	13.2	3.9
150	172	91.6	44.2	23.3	56.6	20.4
200	330	202	93.8	52.6	135	57.0
250	528	357	165	97.0	248	117
280	663	471	218	131	332	166
290	711	512	238	144	363	184
300	759	555	258	158	396	203

Solution. Interpolation of the data given above yields

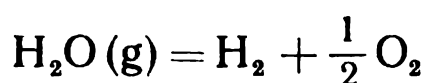
$$\Delta H_0^\circ = \Delta H_{298}^\circ - \int_0^{298} \Delta C_p dT = -26700 - (2 \times 389 - 749 - 254) = -26485 \text{ cal/mol}$$

Next by Eq. (9.11) we find

$$\Delta G_{298}^\circ = -26485 - (2 \times 199 - 546 - 155) = -26182 \text{ cal/mol}$$

Using the tabulated data to perform similar calculations for other temperatures, we get a temperature dependence of ΔH° and ΔG° (Fig. 60).

2. Calculate the equilibrium of the reaction



with the aid of Eqs. (9.12), (9.13) and (9.14) at $T=1000, 1500, 2000, 2500$ and 3000 K according to the data given in Table 15.

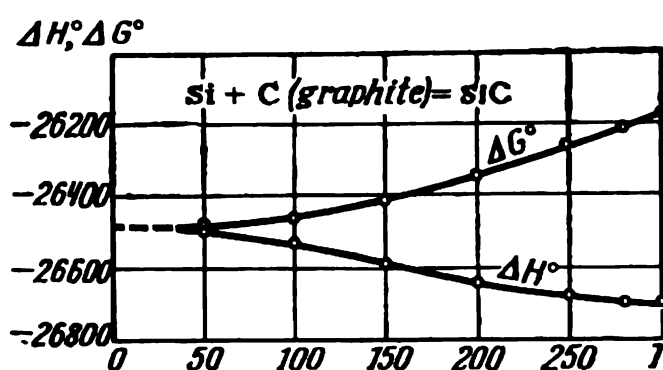


Fig. 60

Table 15

Substance	j	i	θ	C_p
H_2	-3.357	1.6	6130	$6.62 + 0.81 \cdot 10^{-3} T$
O_2	0.533	2.8	2224	$6.26 + 2.746 \times 10^{-3} T - 0.770 \times 10^{-6} T^2$
H_2O	-1.775	3.6	2290, 5730 5510	$8.22 + 0.15 \times 10^{-3} T + 1.34 \times 10^{-6} T^2$

The heat of the reaction at 25°C is 57798 cal/mol.

Solution. 1. We calculate the value of ΔH_0° by Eq. (2.24). Since T is small, θ/T is very big and the last term of Eq. (2.14) may be neglected. Consequently the equation $\Delta H = f(T)$ becomes

$$\Delta H_{298}^\circ = \Delta H_0^\circ + 298.2 \Delta C_p$$

or

$$57798 = \Delta H_0^\circ + 298.2 (6.96 + 0.5 \times 6.96 - 7.95)$$

whence $\Delta H_0^\circ = 57056$ cal/mol.

The second term of Eq. (9.12) equals $1.253 \log T$. We calculate the third term containing the algebraic sum of the integrals

$$\int_0^T \frac{dT}{T^2} \int_0^T (C_p)_{f(T)} dT$$

according to the data given in Appendix 3. The last term of the equation

$$\Delta j = [(-3.357) + 0.5 \times 0.533] - (-1.775) = -1.315$$

Thus, for the dissociation of steam Eq. (9.12) becomes

$$\begin{aligned} \log K_p = & -\frac{12468}{T} + 1.253 \log T + \frac{1}{4.576} \times \\ & \times \left\{ \int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{6130}{T}\right) dT + \frac{1}{2} \int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{2224}{T}\right) dT - \right. \\ & - \left[\int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{2290}{T}\right) dT + \int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{5370}{T}\right) dT + \right. \\ & \left. \left. + \int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{5510}{T}\right) dT \right] \right\} - 1.315 \end{aligned} \quad (a)$$

We determine the values of the integrals according to Appendix 3. Thus, at $T=1000$ K we have

$$\begin{aligned} \left(\frac{\Theta}{T}\right)_{O_2} &= 2.224 \\ \int_0^T \frac{dT}{T^2} \int_0^T f\left(\frac{2224}{T}\right) dT &= 0.228 \end{aligned}$$

2. We transform the expressions $(C_p)_i = f(T)$ to the form

$$C_p = 3.5 + bT$$

We choose $T=1000$ K for the transformation. Hence

$$b = \frac{(C_p)_{1000} - 3.5}{1000}$$

Having calculated b for H_2 , O_2 and H_2O (g), we get

$$\begin{aligned} (C_p)_{H_2} &= 3.5 + 3.93 \cdot 10^{-3} T \\ (C_p)_{O_2} &= 3.5 + 4.74 \cdot 10^{-3} T \\ (C_p)_{H_2O}^g &= 3.5 + 6.21 \cdot 10^{-3} T \end{aligned}$$

Hence by the equation $\Delta H^\circ = f(T)$ we get

$$\Delta H^\circ = 57\,798 - 3.5 \times 0.5 \times 298.2 - 0.5 (3.93 + 0.5 \times 4.74 - 6.21) \times 10^{-3} \times 298.2^2 = 57\,272 \text{ cal/mol.}$$

In accordance with the data given in the initial conditions, Eq. (9.13) takes the form

$$\log K_p = -\frac{12\,516}{T} + 0.875 \log T + 0.009\,836 \times 10^{-3} T - 0.6 \quad (\text{b})$$

3. Equation (9.14) becomes

$$\log K_p = -\frac{12\,631}{T} + 0.875 \log T - 0.6 \quad (\text{c})$$

The results of the calculations using the found equations are given below:

$T, \text{ K}$	1000	1500	2000	2500	3000
$-\log K_p$:					
by Eq. (a)	10.05	5.72	3.53	2.24	1.34
by Eq. (b)	10.50	6.18	3.99	2.66	1.76
by Eq. (c)	10.61	6.24	4.03	2.68	1.77
by Eq. (c) with $\Delta i = -0.12$	10.13	5.76	3.55	2.20	1.29
according to experimental data	10.06	5.73	3.52	2.21	1.31

The last line gives the most accurate values, a comparison with which shows the mean error, namely, 0.9% for Eq. (a), 15.5% for Eq. (b) and 17% for Eq. (c). The substitution of $\Delta i = -0.12$ for -0.6 in Eq. (c) gives good results (the mean error dropped to 0.8%).

3. Calculate the standard entropy of liquid and gaseous 2,2-dimethyl butane according to the dependence of the heat capacity (in cal/mol·K) on the temperature, to the heats and temperatures of phase transitions (see Table 16).

Table 16

$T, \text{ K}$	C_p	$T, \text{ K}$	C_p	$T, \text{ K}$	C_p	$T, \text{ K}$	C_p
20	3.08	100	18.67	160	32.67	230	39.49
30	6.28	110	20.24	170	33.01	240	40.25
40	8.69	120	21.83	174.16 ^e	138.5 ^f	250	41.05
50	10.67	126.81 ^a	1289.2 ^c	180	36.08	260	41.91
60	12.41	130	30.36	190	36.72	270	42.81
70	13.95	140	31.18	200	37.35	280	43.73
80	15.49	140.88 ^b	67.7 ^d	210	37.99	290	44.67
90	17.09	150	32.35	220	38.71		

^a $T_{\text{tr}}^{\text{III-II}}$; ^b $\Delta H_{\text{tr}}^{\text{III-II}}$; ^c $T_{\text{tr}}^{\text{II-I}}$; ^d $\Delta H_{\text{tr}}^{\text{II-I}}$; ^e T_{fus} ; ^f ΔH_{fus}

The temperature dependence of the heat of vaporization within the interval from 270 to 340 K is expressed by the equation

$$\Delta H_{\text{vap}} = 10\,051 - 11.5\,T$$

Also use for the solution the critical parameters ($T_{\text{cr}} = 216.2\text{ K}$ and $p_{\text{cr}} = 30.67\text{ atm}$) and the temperature dependence of the saturated

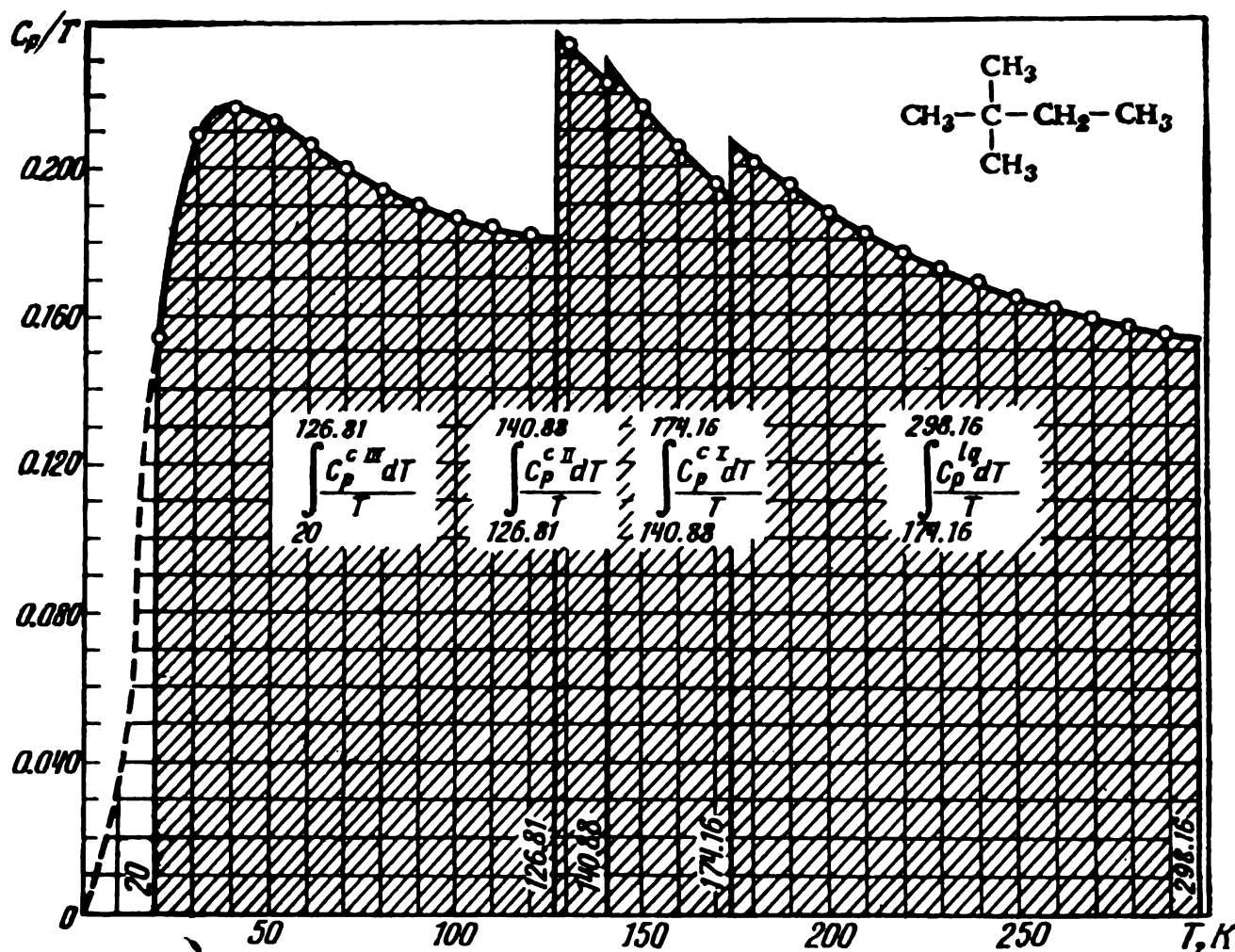


Fig. 61

vapour pressure (in mm Hg) within the interval from -80 to 120°C :

$$\log p = 6.754\,83 - \frac{1081.176}{229.343 + t}$$

Solution. By Eq. (9.15) we have

$$\begin{aligned}
 S_{298}^{\text{lg}} = & \int_0^{20} \frac{C_p^{c, \text{III}}}{T} dT + \int_{20}^{126.81} \frac{C_p^{c, \text{III}}}{T} dT + \frac{1289.2}{126.81} + \\
 & + \int_{126.81}^{140.88} \frac{C_p^{c, \text{II}}}{T} dT + \frac{67.7}{140.88} + \int_{140.88}^{174.16} \frac{C_p^{c, \text{I}}}{T} dT + \frac{138.5}{174.16} + \int_{174.16}^{298.16} \frac{C_p^{\text{lg}}}{T} dT
 \end{aligned}$$

After transforming the values of C_p into C_p/T and plotting a chart in the coordinates C_p/T versus T , we find the integral terms (see

Fig. 61)

$$S_{298}^g = S_{298}^{lq} + \frac{10\,051 - 11.5 \times 298.2}{298.2}$$

To find $(S_{298}^\circ)^g$, it is necessary to introduce a correction for diversion of the vapour from the state of an ideal gas (at p_{298}) and reduce the values obtained to $p=1$ atm.

The results of the calculations are given below:

$S_{20}^{c, III} - S_0^{c, III}$ [graphical integration (extrapolation)]	1.15
$S_{126.81}^{c, III} - S_{20}^{c, III}$ (graphical integration)	20.95
$\Delta S_{tr}^{III-II} = S_{126.81}^{c, III} - S_{126.81}^{c, II}$	10.17
$S_{140.88}^{c, II} - S_{126.81}^{c, III}$ (graphical integration)	3.23
$\Delta S_{tr}^{II-I} = S_{140.88}^{c, II} - S_{140.88}^{c, I}$	0.48
$S_{174.16}^{c, I} - S_{140.88}^{c, II}$ (graphical integration)	6.91
$\Delta S_{fus} = S_{174.16}^{lq} - S_{174.16}^{c, I}$	0.80
$S_{298}^{lq} - S_{174.16}^{lq}$	21.36
$\Delta S_{vap} = S_{298, p=315.7 \text{ mm}}^{g, real} - S_{298}^{lq}$	22.21
$S_{298, p=315.7 \text{ mm}}^{g, ideal} - S_{298, p=315.7 \text{ mm}}^{g, real} = \frac{27 \times 1.987 \times 489.4^3}{32 \times 298.16^3 \times 30.67}$	0.24
$(S_{298}^\circ)^g - S_{298, p=315.7 \text{ mm}}^{g, ideal} = R \ln \frac{315.7}{760}$	-1.75

Summation of the first eight terms gives $S_{298}^{lq} = 65.05$ cal/mol·K.

Summation of all the terms gives $(S_{298}^\circ)^g = 85.75$ cal/mol·K.

4. Find the standard entropy of carbon monoxide. Use the data given in Example 6 of Sec. 2.3 (p. 38) for the calculations.

Solution. By Eq. (9.16) we have

$$\begin{aligned} S_{298}^\circ &= \frac{3}{2} \times 4.576 \log 28.01 + \frac{5}{2} \times 4.576 \log 298.2 + \\ &\quad + 4.576 \log 113.31 + \frac{1.987 \times 46.19 \times 10^{-13}}{1.380 \times 10^{-16} \times 298.2 \times 113.31} - \\ &\quad - 2.313 = 9.934 + 28.309 + 9.405 + 1.968 - 2.313 = \\ &\quad = 47.30 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

5. Calculate the standard entropy of ethylene if $\sqrt[3]{I_A I_B I_C} = 17.33 \times 10^{-40} \text{ g}^3 \text{cm}^6$, $\sigma = 4$ and $\Theta = 1186, 1350, 1366$ (2), 1581, 1929, 2076, 2333, 4295, 4340, 4412 and 4461.

Solution. We use Eq. (9.18) for calculations in accordance with the data given in the initial conditions:

$$\begin{aligned} (S_{298}^\circ)_{eth} &= 4 \times 4.576 \log 298.2 + \frac{3}{2} \times 4.576 \log 28.052 + \\ &\quad + \frac{1}{2} \times 4.576 \log (17.33 \times 10^{-40})^3 - 4.576 \log 4 + \\ &\quad + S_{osc}^\circ + 265.329 = 45.294 + 9.937 - 266.08 - 2.755 + \\ &\quad + S_{osc}^\circ + 265.329 = S_{osc}^\circ + 51.73 \end{aligned}$$

where

$$S_{\text{osc}}^{\circ} = \sum_1^{12} \left[\frac{\Theta/T}{e^{\Theta/T} - 1} - \ln(1 - e^{-\Theta/T}) \right]$$

S_{osc}° is determined with the aid of the following data:

Θ	1186	1350	1366 (2)	1581	1929	2076	2333	4295
Θ/T	3.977	4.527	4.581	5.302	6.469	6.962	7.825	14.404
$(S_{\text{osc}}^{\circ})_i$	0.189	0.123	2×0.115	0.063	0.023	0.015	0.007	0.000

Consequently

$$\sum (S_{\text{osc}}^{\circ})_i = 0.65 \quad \text{and} \quad (S_{298}^{\circ})_{\text{eth}} = 51.73 + 0.65 = 52.38 \text{ cal/mol} \cdot \text{K}$$

6. Find the equation $\Delta G^{\circ} = f(T)$ and ΔG_{1000}° for the reaction

$$6\text{C} + 3\text{H}_2 = \text{C}_6\text{H}_6(\text{g})$$

if for liquid benzene we have $\Delta G_{298}^{\circ} = 29\,731 \text{ cal/mol}$, the saturated vapour pressure of benzene at 25°C is 94.5 mm Hg and $(\Delta H_{\text{vap}})_{\text{benz}} = 8040 \text{ cal/mol}$.

Use the data given in Table 17 for the calculations.

Table 17

Substance	S_{298}°	$(\Delta H_{298}^{\circ})_{\text{comb}}$	C_p
C	1.36	—94 052	$-2.01 + 13.49 \times 10^{-3} T - 6.39 \times 10^{-6} T^2$
H ₂	31.23	—68 310	$6.744 + 2.774 \times 10^{-3} T - 0.1956 \times 10^{-6} T^2$
C ₆ H ₆ (g)	41.49 *	—780 980 *	$-5.04 + 95.63 \times 10^{-3} T - 40.6 \times 10^{-6} T^2$

* Relates to C₆H₆ (lq).

Solution. For gaseous benzene we have

$$\Delta G_{298}^{\circ} = 29\,731 - RT \ln \frac{94.5}{760} = 30\,966 \text{ cal/mol}$$

We determine the same quantity by the equation

$$\Delta G_{298}^{\circ} = \Delta H_{298}^{\circ} - 298 \Delta S_{298}^{\circ}$$

According to Hess's law

$$\Delta H_{298}^{\circ} = 6(-94\,052) + 3(-68\,310) - (-780\,980) + 8040 = 19\,778 \text{ cal/mol}$$

$$\begin{aligned} (S_{298}^{\circ})_{\text{benz}}^{\text{g}} &= (S_{298}^{\circ})_{\text{benz}}^{\text{lq}} + \frac{\Delta H_{\text{vap}}}{T_b} + R \ln \frac{p_1}{p_2} = \\ &= 41.49 + \frac{8040}{298.2} + 4.576 \log \frac{94.5}{760} = 64.31 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

and by Eq. (9.19)

$$\Delta G_{298}^{\circ} = 19\,778 - 298.2 (64.31 - 6 \times 1.36 - 3 \times 31.23) = 30\,972 \text{ cal/mol}$$

which practically coincides with the previously found value.

From the equation $\Delta H^{\circ} = f(T)$ we determine ΔH_0° , namely,

$$\begin{aligned} \Delta H_0^{\circ} &= 19\,778 + 13.212 \times 298.2 - 3.184 \times 10^{-3} \times 298.2^2 + \\ &\quad + 0.558 \times 10^{-6} \times 298.2^3 = 23\,450 \text{ cal/mol} \end{aligned}$$

By Eq. (9.7) we calculate I :

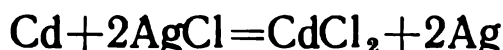
$$\begin{aligned} 30\,972 &= 23\,450 + 13.212 \times 298.2 \ln 298.2 - 3.184 \times \\ &\quad \times 10^{-3} \times 298.2^2 + 0.279 \times 10^{-6} \times 298.2^3 + 298.2 I \end{aligned}$$

whence $I = -49.15$. Consequently

$$\Delta G^{\circ} = 23\,450 + 13.212T \ln T - 3.184 \times 10^{-3}T^2 + 0.279 \times 10^{-6}T^3 - 49.15T$$

whence $\Delta G_{1000}^{\circ} = 62\,670 \text{ cal/mol}$.

7. The e.m.f. of a cell operating at the expense of the reaction



at 25°C is 0.6753 V . Find ΔG_{298}° .

Compare the result with the value calculated according to the standard values given below:

Substance	Cd	AgCl	CdCl ₂	Ag
ΔH_{298}° , cal/mol	0	-30 300	-93 100	0
S_{298}° , cal/mol·K	12.3	23.0	31.16	10.20

Solution. In accordance with Eq. (9.9) we have

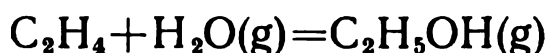
$$\Delta G^{\circ} = -23\,066 \times 2 \times 0.6753 = -31\,150 \text{ cal/mol}$$

which differs from the value

$$\begin{aligned} \Delta G^{\circ} &= [-93\,100 - 2(-30\,300)] - 298.2 [(2 \times 10.20 + 31.16) - \\ &\quad - (12.3 + 2 \times 23.01)] = -32\,500 - 298.2(-6.74) = \\ &\quad = -30\,490 \text{ cal/mol} \end{aligned}$$

found according to Eq. (9.19) by 2.2%.

8. On the basis of the data given in the initial conditions of Problem 9 (p. 240), find ΔG_{473}° and $(K_p)_{473}$ for the reaction



assuming that $\Delta C_p = (\Delta C_p)_{298} = \text{const}$ if at $T = 298 \text{ K}$ the values of C_p are $10.41 \text{ cal/mol} \cdot \text{K}$ for ethylene, 8.025 for steam and 15.4 for gaseous ethyl alcohol.

Solution. Since

$$(\Delta C_p)_{298} = 15.4 - 10.41 - 8.025 = -3.03 \text{ cal/mol} \cdot \text{K}$$

then by Eq. (9.21) we get

$$\Delta G^\circ = -11\,208 + 31.22T - 3.03\,M_0T.$$

From Appendix 10 we find by interpolation that for $T=473.2\text{ K}$ the constant $M_0 \approx 0.0919$. Consequently

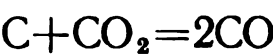
$$\Delta G_{473}^\circ = -11\,208 + 14\,773 + 132 = 3697\text{ cal/mol}$$

and

$$\log (K_p)_{473} = \frac{-3697}{4.576 \times 473.2} = -1.707 = \bar{2}.293$$

Hence $(K_p)_{473} = 1.96 \times 10^{-2}$.

9. Find ΔG° for the reaction



at $T=400, 800$ and 1200 K . Use the data given in Table 18 for the calculations.

Table 18

$T, \text{ K}$	$S^\circ, \text{ cal/mol}\cdot\text{K}$			$\Delta H^\circ, \text{ cal/mol}$			$C_p, \text{ cal/mol}\cdot\text{K}$		
	C	CO ₂	CO	C	CO ₂	CO	C	CO ₂	CO
298.16	1.6609	51.061	47.301	0	−94 052	−26 416	1.449	8.874	6.965
300							1.466	8.894	6.965
600							4.03	11.311	7.276
1200							5.42	13.49	8.167

Base the calculations on the following assumptions:

(1) $\Delta C_p=0$; (2) $\Delta C_p=(\Delta C_p)_{298}$ and (3) the mean values $\Delta \bar{C}_p$ are equal to:

within the interval from 300 to 600 K . $(\Delta \bar{C}_p) = \frac{1}{2} [(\Delta C_p)_{300} + (\Delta C_p)_{600}]$

within the interval from 600 to 1200 K . $(\Delta \bar{C}_p) = \frac{1}{2} [(\Delta C_p)_{600} + (\Delta C_p)_{1200}]$

within the interval from 1200 to 2400 K . $(\Delta \bar{C}_p) = \frac{1}{2} [(\Delta C_p)_{1200} + (\Delta C_p)_{2400}]$

Using the mean values, introduce the following quantities (second averaging):

$T = 300\text{-}450$

\dots

$T = 450\text{-}550$

\dots

$T = 550\text{-}1100$

\dots

$T = 1100\text{-}1500$

\dots

$T = 1500\text{-}2000$

\dots

$a_1 = (\Delta C_p)_{300}$

$a_2 = \frac{1}{2} (a_1 + a_3)$

$a_3 = (\Delta \bar{C}_p)_{300\text{-}600}$

$a_4 = \frac{1}{2} (a_3 + a_5)$

$a_5 = \frac{1}{2} [a_3 + (\Delta \bar{C}_p)_{600\text{-}1200}]$

Take the value of M_0 from Appendix 10.

Compare the results of the calculations with the exact values of ΔG° determined on the basis of the results of solving Example 11 (p. 219).

Solution. 1. At $\Delta C_p = 0$, Eq. (9.20) becomes

$$\Delta G^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ$$

Since

$$\Delta H_{298}^\circ = 2(-26\,416) - (-94\,052) = 41\,220 \text{ cal/mol}$$

and

$$\Delta S_{298}^\circ = 2 \times 47.301 - (1.6609 + 51.061) = 41.880 \text{ cal/mol} \cdot \text{K}$$

then

$$\Delta G^\circ = 41\,220 - 41.880 T \quad (\text{a})$$

whence $\Delta G_{400}^\circ = 24\,468$, $\Delta G_{800}^\circ = 7716$ and $\Delta G_{1200}^\circ = -9036$ cal/mol.

2. If it is assumed that $\Delta C_p = (\Delta C_p)_{298}$, then Eq. (9.21) becomes

$$\Delta G^\circ = \Delta H_{298}^\circ - T \Delta S_{298}^\circ - M_0 \Delta a T$$

Since

$$(\Delta C_p)_{298} = 2 \times 6.965 - 1.449 - 8.874 = 3.607 \text{ cal/mol} \cdot \text{K}$$

then

$$\Delta G^\circ = 41\,220 - 41.880 T - 3.607 \cdot M_0 T \quad (\text{b})$$

Therefore

$$\Delta G_{400}^\circ = 41\,220 - 41.880 \times 400 - 3.607 \times 0.0392 \times 400 = 24\,411 \text{ cal/mol}$$

$$\Delta G_{800}^\circ = 41\,220 - 41.880 \times 800 - 3.607 \times 0.3597 \times 800 = 6678 \text{ cal/mol}$$

$$\begin{aligned} \Delta G_{1200}^\circ &= 41\,220 - 41.880 \times 1200 - 3.607 \times 0.6410 \times 1200 = \\ &= -11\,811 \text{ cal/mol} \end{aligned}$$

3. The average values of ΔC_p are

$$\begin{aligned} (\Delta \bar{C}_p)_{300-600} &= \frac{1}{2} [(2 \times 6.965 - 1.466 - 8.894) + \\ &\quad + (2 \times 7.276 - 4.03 - 11.311)] = \\ &= \frac{1}{2} [3.570 + (-0.789)] = 1.3905 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

$$\begin{aligned} (\Delta \bar{C}_p)_{600-1200} &= \frac{1}{2} [(2 \times 7.276 - 4.03 - 11.311) + \\ &\quad + (2 \times 8.167 - 5.42 - 13.49)] = \\ &= \frac{1}{2} [(-0.789) + (-2.576)] = -1.6825 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

hence

$$\begin{aligned} a_1 &= 3.570 \\ a_3 &= 1.3905 \\ a_2 &= \frac{1}{2} (3.570 + 1.3905) = 2.480\,25 \\ a_5 &= \frac{1}{2} [1.3905 + (-1.6825)] = -0.146 \\ a_4 &= \frac{1}{2} [1.3905 + (-0.146)] = 0.622\,25 \end{aligned}$$

Using the found values of a_i , we get for the interval from 300 to 450 K

$$\Delta G^\circ = 41\,220 - 41.880T - 3.570M_0T \tag{c'}$$

whence

$$\Delta G^\circ_{400} = 41\,220 - 41.880 \times 400 - 3.570 \times 0.0392 \times 400 = 24\,412 \text{ cal/mol}$$

for the interval from 550 to 1100 K

$$\Delta G^\circ = 41\,220 - 41.880T - 1.3905M_0T \tag{c''}$$

whence

$$\Delta G^\circ_{800} = 41.220 - 41.880 \times 800 - 1.3905 \times 0.3597 \times 800 = 7316 \text{ cal/mol}$$

for the interval from 1100 to 1500 K

$$\Delta G^\circ = 41\,220 - 41.880T + 0.622\,25M_0T \tag{c'''}$$

whence

$$\begin{aligned} \Delta G^\circ_{1200} &= 41\,220 - 41.880 \times 1200 - 0.622\,25 \times 0.6410 \times 1200 = \\ &= -9515 \text{ cal/mol} \end{aligned}$$

Table 19 contains the results of the calculations and gives the values of ΔG obtained on the basis of the results of solving Example 11.

Table 19

Equation	T		
	400	800	1200
(a)	24 468	7716	—9036
(b)	24 411	6678	—11811
(c'), (c''), (c''')	24 412	7316	—9515
Exact calculation	24 311	7185	—9645

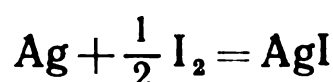
Problems

1. Use Eq. (9.10) to find the temperature of changing of rhombic sulphur into monoclinic sulphur if for this process

$$\Delta H=50.4+3.69\times 10^{-4}T^2$$

Compare the result with the experimentally found value (368.6 K).

2. On the basis of the reference data given in Table 20, calculate ΔG_{298}° for the reaction



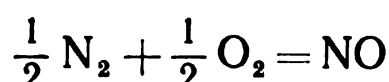
if $\Delta H_{298}^{\circ}=-15\,100\text{ cal/mol}$.

Table 20

T	Ag		$\frac{1}{2} \text{I}_2$		$\frac{1}{2} \text{AgI}$	
	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$	$\int_0^T C_p dT$	$T \int_0^T \frac{dT}{T^2} \int_0^T C_p dT$
20	1.84	0.61	11	5	14	8
50	47.0	19.6	124	78	99	79
100	243	154	390	379	366	342
200	785	722	973	1368	926	1243
250	1077	1164	1287	1989	1234	1820
280	1257	1449	1482	2391	1421	2198
290	1316	1546	1548	2530	1485	2328

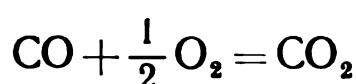
Use Eq. (9.11) for the calculations.

3. With the aid of Eq. (9.11), calculate $\log K_p$ for the reaction



at $T=2000\text{ K}$ if $\Delta H_{298}^{\circ}=21\,600\text{ cal/mol}$, $\Theta_{\text{N}_2}=3350$, $\Theta_{\text{O}_2}=2224$, $\Theta_{\text{NO}}=2705$, $j_{\text{NO}}=0.55$, $j_{\text{N}_2}=-0.153$ and $j_{\text{O}_2}=0.547$.

4. Use Eq. (9.13) to calculate $\log K_p$ for the reaction



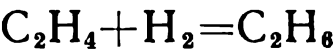
within the interval from 300 to 1500 K (every 300 kelvins) if $\Delta H_{298}^{\circ}=-67\,636\text{ cal/mol}$, $i_{\text{CO}_2}=3.2$, $i_{\text{CO}}=3.5$, $i_{\text{O}_2}=2.8$ and at $t=900^{\circ}\text{C}$ we have $(C_p)_{\text{CO}_2}=12.678\text{ cal/mol}\cdot\text{K}$, $(C_p)_{\text{CO}}=7.787$ and $(C_p)_{\text{O}_2}=8.212\text{ cal/mol}\cdot\text{K}$.

Compare the results with the values given below:

$T, \text{ K}$	300	600	900	1200	1500
$\log K_p$	45.05	20.06	11.84	7.74	5.29

5. Find the temperature at which the pressure of dissociation of MgCO_3 and CdCO_3 equals one atmosphere if the standard heats of formation of MgCO_3 , CdCO_3 , MgO , CdO and CO_2 are respectively -266.6 , -182 , -146.1 , -62.36 and -94.03 kcal/mol and $i_{\text{CO}_2}=3.2$. Compare the results of the calculation with the experimentally found values of the relevant temperature of dissociation equal to 815 K for MgCO_3 and 617 K for CdCO_3 .

6. The standard heats of formation of gaseous ethylene and ethane are 12.496 and -20.236 kcal/mol, respectively. The conditional chemical constants for C_2H_4 , H_2 and C_2H_6 are respectively equal to 2.8, 1.6 and 2.6. What form will Eq. (9.14) take on for the reaction



Use the equation found to calculate $\log (K_p)_{773}$. Compare the results with the value of $(K_p)_{773}=2.50$.

7. On the basis of the data given in Table 21 calculate the standard entropy of ethane.

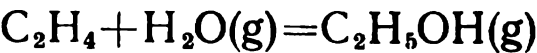
Table 21

T	C_p	T	C_p	T	C_p
15	0.66	80	12.72	184.1***	3514****
20	1.59	90*	686.90**	189.1	10.45
30	3.59	100	16.38	209.5	10.69
40	5.94	120	16.55	229.6	11.02
50	7.81	140	16.69	249.9	11.47
60	9.45	160	16.93	272.0	12.01
70	11.09	180	17.26	292.0	12.57

* T_{fus} ; ** ΔH_{fus} ; *** T_{b} ; **** ΔH_{vap} .

8. Calculate the standard entropy of hydrogen sulphide if $I_{\text{A}}I_{\text{B}}I_{\text{C}}=49.5 \times 10^{-120} \text{ g}^3\text{cm}^6$, $\sigma=2$, $\Theta=1812.5$ and 3768.5 (2).

9. Find K_p at $t=200^\circ\text{C}$ for the reaction of hydration of ethylene



The properties of the reagents are given in Table 22.

Compare the results of the calculations with the value of $K_{473}=1.74 \times 10^{-2}$ (the average of experimental data). Use Eq. (9.7) for the calculation.

Table 22

Substance	S_{298}°	$(\Delta H_{\text{form}}^\circ)_{298}$	C_p
C ₂ H ₅ OH(g)	66.39	−56 510	$2.16+49.7\times10^{-3}T-15.53\times10^{-6}T^2$
C ₂ H ₄	52.48	12 496	$2.08+31.1\times10^{-3}T-10.66\times10^{-6}T^2$
H ₂ O(g)	45.13	−57 798	$7.55+1.3525\times10^{-3}T+0.8658\times10^{-6}T^2$

10. Find ΔG_{298}° and K_{298} for the reaction

$$\text{BaSO}_4(\text{c}) = \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$

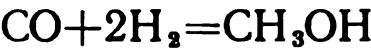
Use the following data for the calculations:

Substance	BaSO ₄ (c)	Ba ²⁺	SO ₄ ^{2−}
ΔH_{298}° , cal/mol	−345 440	−128 360	−215 800
S_{298}° , cal/mol·K	31.6	2.3	4.4

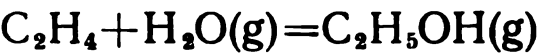
11. The equation

$$\log K_p = \frac{3925}{T} - 9.840 \log T + 3.47 \times 10^{-3}T + 14.80$$

was proposed for the reaction

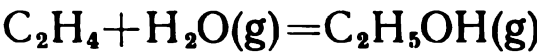


- (1) Determine ΔG° at 390 °C and compare it with the value found on the basis of spectroscopic data (see the initial conditions of Example 4 on p. 247).
- (2) Calculate ΔG_{298}° , ΔH_{298}° and S_{298}° for methanol and compare the values obtained with the most authentic ones equal respectively to −39 060 cal/mol, −48 490 cal/mol and 57.72 cal/mol·K. Use the following values for the calculations: $(\Delta G_{298}^\circ)_{\text{CO}} = -32\,810$ cal/mol, $(\Delta H_{298}^\circ)_{\text{CO}} = -26\,416$ cal/mol, $(S_{298}^\circ)_{\text{H}_2} = 31.23$ and $(S_{298}^\circ)_{\text{CO}} = 47.32$ cal/mol·K.
12. On the basis of the data given in the initial conditions of Problem 9, find the equation of the temperature dependence of the equilibrium constant for the reaction



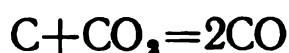
assuming that $\Delta C_p = 0$.

13. On the basis of the data given in the initial conditions of Problem 9, find K_{473} for the reaction



Use the Temkin and Shwartsman method for the calculations.

14. Use Eq. (9.21) to find the equilibrium constant of the reaction



at $T=400, 800$ and 1200 K if

$$(C_p)_{\text{CO}} = 6.887 + 0.5935 \times 10^{-3}T + 0.462 \times 10^{-6}T^2$$

$$(C_p)_{\text{C}} = -2.01 + 13.49 \times 10^{-3}T - 6.39 \times 10^{-6}T^2$$

$$(C_p)_{\text{CO}_2} = 5.372 + 12.404 \times 10^{-3}T - 4.78 \times 10^{-6}T^2$$

Take the values of the quantities needed for the calculations from the initial conditions of Example 9 and Appendix 10.

Compare the results with the exact value (see the solution of Example 11 of Sec. 9.1, p. 219) and the results of solving Example 9.

15. In studying the temperature dependence of the e.m.f. of the cell

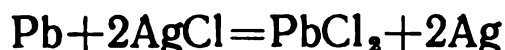


the following data were obtained: $E_{298} = 0.54754$, $E_{298} = 0.54452$ and $E_{308.2} = 0.54149$ V.

Determine: (1) ΔG_{298}° ; (2) $(S_{298}^\circ)_{\text{CdS}}$. Use the following data for the calculations: $(\Delta G_{298}^\circ)_{\text{CdS}} = -33100$ and $(\Delta G_{298}^\circ)_{\text{H}_2\text{S}} = -7870$ cal/mol; $(S_{298}^\circ)_{\text{Cd}} = 12.3$, $(S_{298}^\circ)_{\text{H}_2\text{S}} = 49.15$ and $(S_{298}^\circ)_{\text{H}_2} = 31.23$ cal/mol·K.

Compare the result with the tabulated value of the entropy equal to 17.0 cal/mol·K.

16. Determine the heat of the reaction



if the e.m.f. of a cell operating at the expense of this process at 25°C is 0.490 V, and the temperature coefficient of the e.m.f. is -0.000186 V/K.

Compare the results with the value found by calculations according to the heats of formation if $(\Delta H_{298}^\circ)_{\text{PbCl}_2} = -85500$ and $(\Delta H_{298}^\circ)_{\text{AgCl}} = -30300$ cal/mol.

17. Use Eq. (9.22) to find the equilibrium constant at 327°C for the reaction



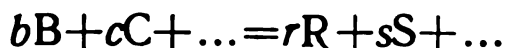
Compare the result with $\log K_p = 3.79$ found by an equation obtained on the basis of experimental data. Use the data given in Appendix 11 for the calculations.

Chapter Ten

EQUILIBRIUM TRANSITION

10.1. CALCULATION OF EQUILIBRIUM TRANSITION

The composition of the equilibrium mixture for the reaction



in the gaseous phase is calculated by the equation

$$K = K_f = \underbrace{\frac{\gamma_R^r \cdot \gamma_S^s \dots}{\gamma_B^b \cdot \gamma_C^c \dots}}_{K_\gamma} \underbrace{\frac{n_R^r \cdot n_S^s \dots}{n_B^b \cdot n_C^c \dots}}_{K_n} \left(\frac{p}{n_R + n_S + \dots + n_B + n_C + \dots + n_{in}} \right)^{\Delta n} \quad (10.1)$$

where γ_i and n_i = activity coefficient and number of moles of each component

n_{in} = number of moles of inert gas

p = total pressure

$\Delta n = (n_R + n_S + \dots) - (n_B + n_C + \dots)$.

The values of γ_i can be found from Fig. 31 (p. 147) and Appendix 9.

At low pressures $K_\gamma = 1$ and $K_f = K_p$, i.e. the equilibrium constant can be expressed through the partial pressures

$$K_p = \frac{p_R^r \cdot p_S^s \dots}{p_B^b \cdot p_C^c \dots} \quad (10.1a)$$

where p_i = partial pressures.

If crystalline or liquid substances participate in a reaction, then their activities (with exponents equal to the stoichiometric coefficients) should be included in Eq. (10.1). In the majority of cases, however, they may be assumed to equal unity. An exception are reactions attended by the formation of solutions, and also reactions in which the pressure and temperature are very high.

If a reaction proceeds in a solution that can be considered an ideal one, then

$$K = \underbrace{\frac{x_R^r \cdot x_S^s \dots}{x_B^b \cdot x_C^c \dots}}_{K_x} \underbrace{\frac{c_R^r \cdot c_S^s \dots}{c_B^b \cdot c_C^c \dots}}_{K_c} \left(\frac{p}{n_B + n_C + \dots + n_R + n_S + \dots} \right)^{\Delta n} \quad (10.2)$$

For solutions of electrolytes, the equilibrium constant is expressed through the activities of the ions. The activity of each ion may be replaced by the product of its concentration and the activity coefficient.

The mean activity coefficient and the molality

$$\gamma_{\pm}^v = \gamma_+^{v+} \cdot \gamma_-^{v-} \quad \text{and} \quad m_{\pm}^v = m_+^{v+} \cdot m_-^{v-}$$

(for the reactions $M_{v+}A_{v-} = v^+M^{z+} + v^-A^{z-}$) are usually used for calculations.

Examples

1. The degree of dissociation of nitrogen tetroxide into nitrogen dioxide at $t=0^\circ\text{C}$ and $p=1$ atm is 11%.

Find the equilibrium constant of this reaction.

Solution. Since the pressure is not great, we have $K_p=1$ and in accordance with Eq. (10.1)

$$K_f = K_p = \frac{n_{\text{NO}_2}^2}{n_{\text{N}_2\text{O}_4}} \left(\frac{1}{n_{\text{NO}_2} + n_{\text{N}_2\text{O}_4}} \right)^{2-1}$$

We shall use the following scheme for calculation of the equilibrium transition (in the following it will be omitted):

Reaction	$\text{N}_2\text{O}_4 = 2\text{NO}_2$
Reactants (moles)	$\begin{matrix} 1 & 0 \end{matrix}$
Equilibrium mixture (moles)	$\begin{matrix} 1-x & 2x \end{matrix}$
	$\underbrace{\hspace{1.5cm}}_{1+x}$

Hence in accordance with the found equation we have

$$K_p = \frac{(2x^2)}{1-x} \frac{1}{1+x} = \frac{4x^2}{1-x^2}$$

Introducing the value of $x=0.11$ given in the initial conditions, we get

$$K_p = \frac{4 \times 0.11^2}{1 - 0.11^2} = \frac{0.0484}{0.9879} = 0.049$$

2. The equation

$$\log K_p = \frac{5660}{T} - 2.961 \log T + 0.7668 \times 10^{-3}T - 0.1764 \times 10^{-6}T^2 + 2.19$$

has been proposed for the reaction of hydrogenation of propylene



Find the content of propane in an equilibrium mixture at $T=800$ K and $p=1$ atm. Perform the calculations on the basis of the following:

(1) the initial mixture consists of one mole of propylene and one mole of hydrogen;

(2) the equilibrium mixture contains $(1-x)$ moles of propane ($\sum n_i = 1$).

Compare the result of the calculations with the most reliable value of $\log K_p = 1.1911$ and show that it does not depend on the method of calculations.

Solution. The calculations are given in Table 23.

Table 23

	First alternative of calculations	Second alternative of calculations
$n_{C_3H_6}$	$1-x$	$\frac{x}{2}$
n_{H_2}	$1-x$	$\frac{x}{2}$
$n_{C_3H_8}$	x	$1-x$
$\sum n_i$	$2-x$	1
$p_{C_3H_6}$	$\frac{(1-x) p}{2-x}$	$\frac{xp}{2}$
p_{H_2}	$\frac{(1-x) p}{2-x}$	$\frac{xp}{2}$
$p_{C_3H_8}$	$\frac{xp}{2-x}$	$(1-x) p$
K_p	$\frac{x(2-x)}{(1-x)^2 p}$	$\frac{4(1-x)}{x^2 p}$
x	$\frac{(pK_p+1) \pm \sqrt{pK_p+1}}{pK_p+1}$	$\frac{-2 \pm 2\sqrt{pK_p+1}}{pK_p}$

Next we find K_p at $T=800$ K:

$$\begin{aligned}
 \log K_p &= \frac{5660}{800} - 2.961 \log 800 + 0.7668 \times 10^{-3} \times \\
 &\quad \times 800 - 0.1764 \times 10^{-6} \times 800^2 + 2.19 = \\
 &= 7.075 - 8.596 + 0.6134 - 0.1129 + 2.19 = 1.1695 \\
 K_p &= 14.77
 \end{aligned}$$

The satisfactory coincidence with the value given in the initial conditions of the example (the discrepancy is 4.9%) points to the accurate nature of the equation.

Inserting the values of $K_p=14.77$ and $p=1$ atm into the equations found for x (see Table 23), we get:

$$(1) \quad x = \frac{(1 \times 14.77 + 1) - \sqrt{1 \times 14.77 + 1}}{1 \times 14.77 + 1} = \frac{15.77 - 3.97}{15.77} = 0.7482$$

i.e. an equilibrium mixture will contain

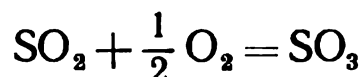
$$\frac{0.7482}{2 - 0.7482} \times 100 = \frac{74.82}{1.2518} = 59.8\% \text{ C}_3\text{H}_8$$

$$(2) \quad x = \frac{-2 + 2 \sqrt{1 \times 14.77 + 1}}{1 \times 14.77} = \frac{-2 + 2 \times 3.97}{14.77} = 0.4022$$

i.e. an equilibrium mixture will contain $(1 - 0.4022) \times 100 = 59.8\%$ of C_3H_8 .

As should be expected, the result of the calculations does not depend on the method used to find it.

3. At what temperature will the theoretical yield of sulphur trioxide according to the reaction



be equal to 90% if the initial gas contains 6% of SO_2 and 12% of O_2 , and the pressure $p=1$ atm?

For the calculations use the approximate equation

$$\Delta G^\circ = -22\,600 + 21.4T$$

Solution. The equilibrium partial pressures are:

$$p_{\text{SO}_3} = (p_{\text{SO}_2})_{\text{in}} y$$

$$p_{\text{SO}_2} = (p_{\text{SO}_2})_{\text{in}} (1 - y)$$

$$p_{\text{O}_2} = (p_{\text{O}_2})_{\text{in}} - 0.5y (p_{\text{SO}_2})_{\text{in}}$$

where y is the degree of oxidation at the moment of equilibrium, while the subscript "in" denotes the initial state of the mixture.

Since at $p=1$ atm we have $K_y=1$, then

$$K_p = \frac{p_{\text{SO}_3}}{p_{\text{SO}_2} p_{\text{O}_2}^{0.5}} = \frac{(p_{\text{SO}_2})_{\text{in}} y}{(p_{\text{SO}_2})_{\text{in}} (1 - y) [(p_{\text{O}_2})_{\text{in}} - 0.5y (p_{\text{SO}_2})_{\text{in}}]^{0.5}}$$

or

$$K_p = \frac{0.06 \times 0.9}{0.06 \times (1 - 0.9) (0.12 - 0.5 \times 0.9 \times 0.06)^{0.5}} = \frac{0.9}{0.1 \times 0.305} = 29.5$$

By equation (9.3) we have

$$\Delta G^\circ = -4.576T \log 29.5 \approx -6.725T$$

In accordance with the temperature dependence of ΔG° given in the initial conditions we get

$$-6.725T = -22\,600 + 21.4T, \text{ whence } T = \frac{22\,600}{28.125} = 803.6 \text{ K}$$

4. Find the yield of methanol at $t=390^\circ\text{C}$ and $p=300 \text{ atm}$ according to the reaction



if $\Delta G_{663.2}^\circ \approx 14\,700 \text{ cal/mol}$. Take the critical parameters from Appendix 8.

Solution. In accordance with Eq. (9.3) we have

$$14\,700 = -4.576 \times 663.2 \log K$$

whence

$$\log K = -4.845 = \bar{5}.155 \text{ and } K = 1.43 \times 10^{-5}$$

We determine the quantity K_γ according to the values of π and τ^* (see Appendix 9).

Substance . . .	CO	H ₂	CH ₃ OH
π	8.67	14.4	3.81
τ	4.93	16.1	1.29
γ	1.143	1.103	0.604

Consequently

$$K_\gamma = \frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}}\gamma_{\text{H}_2}^2} = \frac{0.604}{1.143 \times 1.103^2} = 0.434$$

In accordance with Eq. (10.1) we have

$$1.43 \times 10^{-5} = 0.434 \frac{x}{(1-x)(2-2x)^2} \left(\frac{300}{3-2x} \right)^{1-3}$$

or

$$\frac{x(3-2x)^2}{(1-x)(2-2x)^2} = 2.97$$

we determine x by the method of trial and error:

$$x = 0.5; \quad \frac{0.5 \times 2^2}{0.5 \times 1^2} = 4.0 \neq 2.97$$

$$x = 0.4; \quad \frac{0.4 \times 2.2^2}{0.6 \times 1.2^2} = 2.24 \neq 2.97$$

$$x = 0.45; \quad \frac{0.45 \times 2.1^2}{0.55 \times 1.1^2} = 2.98 \approx 2.97$$

* For H₂ we take $p_{\text{cr}} + 8$ and $T_{\text{cr}} + 8$.

We finally assume that $x=0.45$. Consequently, the yield of methanol is

$$\frac{0.45}{3-2 \times 0.45} \times 100 = 21\%$$

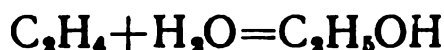
5. It is proposed to calculate the activity coefficient of a component of a gas mixture (γ_i) on the basis of Eq. (4.2). Hence, combining the equation

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

and Eq. (4.2), we get

$$\ln \gamma_i = \frac{9\pi_i}{128\tau_i} \left(1 - \frac{6}{\tau_i^2}\right)$$

Use this equation to calculate the value of K_γ for the reaction



at $t=350^\circ\text{C}$ and $p=100$ atm and determine K_p if $K_f=0.00135$.

Compare the result of the calculations with the value of $K_p=0.00149$.

Solution. In accordance with the equation given in the initial conditions of the example and the values of t_{cr} and p_{cr} (Appendix 8) we have:

$$\begin{aligned} \log \gamma_{\text{C}_2\text{H}_4} &= \frac{9 \times 100 \times 282.9}{2.303 \times 128 \times 50.8 \times 623.2} \left(1 - \frac{6 \times 282.9^2}{623.2^2}\right) = \\ &= -0.00645 = \bar{1}.99355 \end{aligned}$$

$$\gamma_{\text{C}_2\text{H}_4} = 0.985$$

$$\begin{aligned} \log \gamma_{\text{H}_2\text{O}} &= \frac{9 \times 100 \times 647.3}{2.303 \times 128 \times 218.5 \times 623.2} \left(1 - \frac{6 \times 647.3^2}{623.2^2}\right) = \\ &= -0.07943 = \bar{1}.92057 \end{aligned}$$

$$\gamma_{\text{H}_2\text{O}} = 0.833$$

$$\begin{aligned} \log \gamma_{\text{C}_2\text{H}_5\text{OH}} &= \frac{9 \times 100 \times 516.2}{2.303 \times 128 \times 63.1 \times 623.2} \left(1 - \frac{6 \times 516.2^2}{623.2^2}\right) = \\ &= -0.1249 = \bar{1}.8751 \end{aligned}$$

$$\gamma_{\text{C}_2\text{H}_5\text{OH}} = 0.750$$

Therefore

$$K_\gamma = \frac{0.750}{0.985 \times 0.833} = 0.914 \quad \text{and} \quad K_p = \frac{K_f}{K_\gamma} = \frac{0.00135}{0.914} = 0.001477$$

The discrepancy between the recommended and the found value of K_p is 0.9%.

6. In studying the pressure of saturated water vapour over molten alkalies (KOH and NaOH) in the presence of carbonates and chlorides of alkali metals, investigators obtained the following data for an initial melt having the composition 93% of KOH and 7% of K_2CO_3 :

p , mm Hg	200	200	200	500	500	500	500
t , °C	340	360	380	340	360	380	400
H_2O , %	6.64	4.95	3.50	10.59	8.48	6.78	5.56

Determine the heat of hydration of potassium hydroxide with water vapour up to a water content of 6%.

Solution. In the equation $\log K=f(1/T)$ for the reaction



we replace the ratio K_2/K_1 with the ratio of the pressures of the saturated vapour at the same water content in the potassium hydroxide (6%). We find the latter quantity by plotting the isobars $p_1=200$ and $p_2=500$ mm Hg in the coordinates temperature versus moisture content. Hence

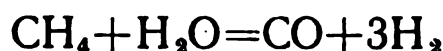
$$\log \frac{500}{200} = \frac{\Delta H}{4.576} \left(\frac{1}{620} - \frac{1}{664} \right)$$

whence

$$\Delta H = \frac{4.576 \times 0.39794 \times 620 \times 664}{44} = 17\,040 \text{ cal/mol}$$

Problems

- Solve Example 2 (p. 244) assuming that
 - the initial system consists of one mole of propane;
 - an equilibrium mixture contains x moles of propane ($\sum n_i=1$).
- Calculations show that when a stoichiometric mixture of methane and steam is heated to $T=1100$ K ($p=1$ atm) provided that the following reaction proceeds



the equilibrium mixture should contain 72.43% of H_2 .

Determine the equilibrium constant for this reaction.

- Using the data given in the initial conditions and the solution of Example 5 (p. 248), find the equilibrium content of alcohol in the water-alcohol condensate formed after cooling the products of hydration of ethylene.

- The equilibrium concentration of NO upon the oxidation of nitrogen with air is equal to:

T , K	2400	3000
NO, volume %	1.50	3.57

- Find the equilibrium constant for the indicated temperatures.
- Calculate the heat of the reaction within the interval of 2400-3000 °C and compare it with $\Delta H_{298}^\circ=21\,600$ cal/mol. What conclusion can be made by comparing the found value of ΔH° with ΔH_{298}° ?

5. The degree of dissociation of steam



and of carbon dioxide



at $T=1500$ K is respectively equal to 2.21×10^{-4} and 4.8×10^{-4} .

Find the equilibrium constant for the reaction



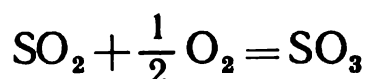
at $T=1500$ K.

Compare the result with the tabulated value (0.37).

6. The equation

$$\Delta G^\circ = -21\,055.7 + 5.618T \ln T - 10.4575 \times 10^{-3}T^2 + \\ + 3.210\,58 \times 10^{-6}T^3 - 11.3653T$$

was proposed for the reaction



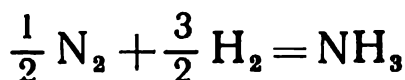
Determine the yield of SO_3 upon the reaction of a stoichiometric mixture of SO_2 and O_2 if $p=1$ atm and $T=700$ K.

7. Using the result obtained in solving Problem 6:

(1) determine the equilibrium composition of the gas and the degree of transition of sulphur dioxide into sulphur trioxide at $p=1$ atm and $T=700$ K if the reaction mixture consists of 7% of sulphur dioxide, 11% of oxygen and 82% of nitrogen;

(2) determine the composition of the gas for the case when the degree of transition is 0.9.

8. Find the yield of ammonia by the reaction



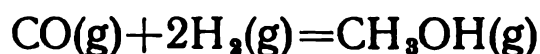
if the ratio of the gases in the mixture is a stoichiometric one, the temperature in the column is 750 K and the pressure is 400 atm.

Use Fig. 62 and the equation

$$\Delta G^\circ = -9070 + 17.388T \log T - 3.978 \times 10^{-3}T^2 + \\ + 0.335 \times 10^{-6}T^3 - 24.55T$$

for the calculations.

9. The values of $f_{\text{CH}_3\text{OH}}/f_{\text{CO}}f_{\text{H}_2}^2$ were calculated for a number of arbitrarily set values of the composition of the gas mixture in the system



The calculations gave the following results ($p=100\text{ atm}$, $t=250^\circ\text{C}$, $[\text{H}_2]:[\text{CO}]=2:1$):

$x_{\text{CH}_3\text{OH}}$	0.91	0.636	0.4
$\frac{f_{\text{CH}_3\text{OH}}}{f_{\text{CO}}f_{\text{H}_2}^2} \times 10^{-4}$	42.22	13.40	6.585

Use these data to determine K_f and K_v if the experimentally found equilibrium yield is 69 mol%.

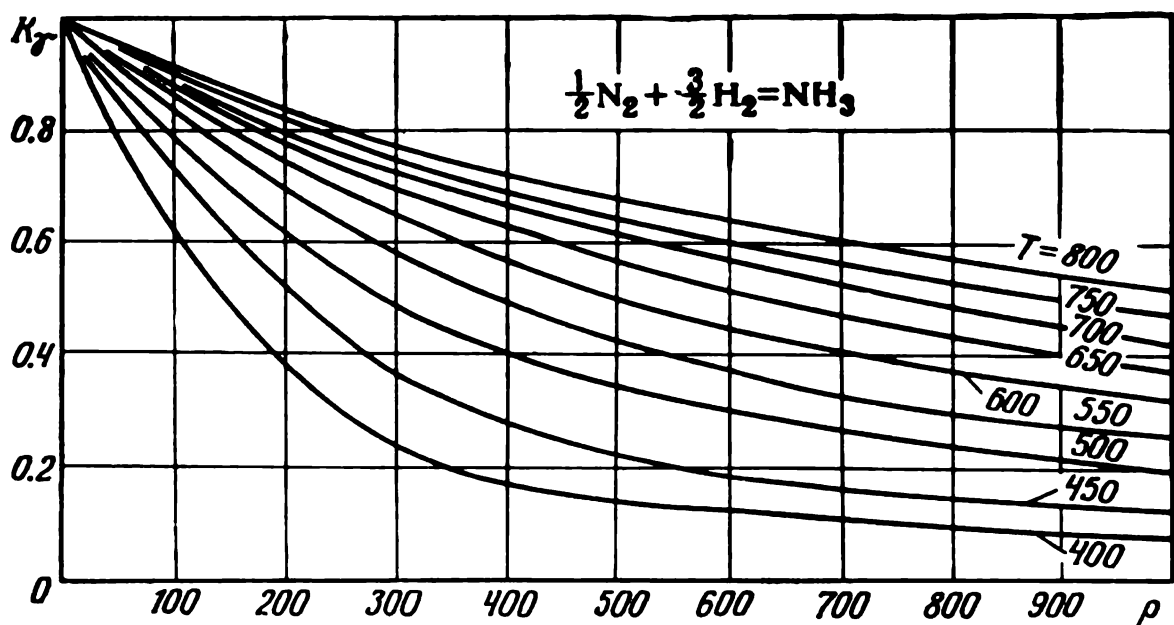
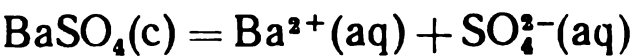


Fig. 62

10. The equilibrium constant at 25°C for the reaction



equals 4.16×10^{-7} [see the solution of Problem 10 in Sec. 9.2 (p. 241)].

Determine the solubility of BaSO_4 in water at 25°C .

Use for the calculations the value of γ_{\pm} found by the equation

$$\log \gamma_{\pm} = -0.509 z^+ z^- \sqrt{I}$$

where z^+ and z^- = charges of ions

I = ionic strength.

Compare the result with the experimentally found value of $q_{298} = 9.57 \times 10^{-6}$.

11. In studying the dissociation of acetic acid vapours and the equilibrium between its aqueous solutions and their vapours, the following values of the partial vapour pressure of the monomer (p_1) and the dimer (p_2) were obtained:

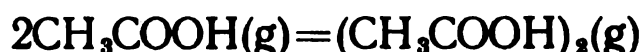
at $t=80.09^\circ\text{C}$

p_1 , mm Hg	9.0	16.0	20.2	28.0	38.0	54.9	56.1
p_2 , mm Hg	3.3	9.0	18.0	33.0	59.6	117.0	152.2

at $t=42.00^\circ\text{C}$

p_1 , mm Hg	1.1	2.7	4.2	4.4	4.6	6.5
p_2 , mm Hg	0.8	3.9	7.0	13.9	26.2	32.0

Determine: (1) the heat of association of acetic acid



(2) the ratio between associated and non-associated molecules at $t=30^\circ\text{C}$.

10.2. INFLUENCE OF VARIOUS FACTORS ON THE EXTENT OF A REACTION

The influence of various factors on the extent of a reaction is determined on the basis of Eq. (10.1). Rewriting it in the form

$$\frac{n_R^r \cdot n_S^s \dots}{n_B^b \cdot n_C^c \dots} = \frac{K}{K_p} \left(\frac{n_B + n_C + \dots + n_R + n_S + \dots + n_{\text{In}}}{p} \right)^{\Delta n} \quad (10.3)$$

we arrive at the conclusion that

(1) an *increase in the temperature* facilitates the course of an endothermal reaction [since in accordance with Eq. (10.3) the value of K grows with the temperature] and lowers the yield of products of an exothermal reaction. At high pressures account must also be taken of the influence of the temperature on K_p ;

(2) *pressure* shifts the equilibrium in the direction of a reduction of the volume;

(3) an *inert gas* has an influence opposite to that of the pressure at a constant composition of the mixture (i.e. it shifts the equilibrium in the direction of an increase in the volume).

An *excess amount of the components* increases the yield of substances that are on the other side of the equal sign in the equation of the reaction.

The question considered above is closely related to that of the *direction of a process*, which is determined by the sign of ΔG . If in the given conditions $\Delta G < 0$, then the reaction is possible. If $\Delta G > 0$, then the reaction is impossible. At $\Delta G = 0$ the system is in equilibrium.

Knowing the value of ΔG° or K (see Chapter Nine), we can calculate ΔG by the equation

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_R^r \cdot a_S^s \dots}{a_B^b \cdot a_C^c \dots} = -RT \ln K + RT \ln \frac{a_R^r \cdot a_S^s \dots}{a_B^b \cdot a_C^c \dots} \quad (10.4)$$

Examples

1. Using the result of solving Example 1 of Sec. 10.1 (p. 244), determine:

(1) by how much the degree of dissociation of nitrogen tetroxide grows at $t=0^\circ\text{C}$ if the pressure is lowered from $p=1$ to $p=0.8$ atm;

(2) to what pressure must the mixture be compressed for the degree of dissociation to reach 8% at 0°C .

Assume in the calculations that K_p does not depend on the pressure.

Solution. 1. In accordance with the result of solving the example indicated above, we have

$$0.049 = \frac{4x^2}{1-x^2} p \quad (\text{a})$$

and at $p=0.8$ atm

$$\frac{4x^2}{1-x^2} = 0.0612$$

whence

$$x = \sqrt{\frac{0.0612}{4.0612}} = 0.123$$

i.e. the degree of dissociation grows by 11.8%.

2. Introducing $x=0.08$ into Eq. (a), we get

$$0.049 = \frac{4 \times 0.08^2}{1-0.05^2} \cdot p = \frac{0.0256p}{0.9975}$$

whence

$$p = \frac{0.049 \times 0.9975}{0.0256} \approx 1.9$$

2. Find the influence of the presence of an inert gas on the equilibrium of the synthesis of ammonia. Perform the calculations for $x_{\text{in}} = 0.08, 0.20$ and 0.40 , assuming in all cases that $[\text{H}_2]:[\text{N}_2]=3:1$, $p=300$ atm and $T=750$ K. In these conditions $K_p=0.75$ and $K=0.00494$ (see Problem 8 on p. 250 and Fig. 62).

Solution. If the calculations are performed from two moles of the initial mixture, then in the given case in accordance with Eq. (10.3) we have

$$\frac{x(2-x)}{(a-0.5x)^{0.5} (b-1.5x)^{1.5}} = \frac{0.00494 \times 300}{0.75} = 1.976$$

where a = number of moles of nitrogen in 2 moles of the mixture

b = number of moles of hydrogen in 2 moles of the mixture.

If $x_{\text{in}} = 0.08$, then

$$\frac{x(2-x)}{(0.46-0.5x)^{0.5} (1.38-1.5x)^{1.5}} = 1.976$$

whence $x \approx 0.42$, which corresponds to $\frac{0.42 \times 100}{2 - 0.42} = 26.6\%$ of NH_3 .

For $x_{\text{in}} = 0.20$ and $x_{\text{in}} = 0.40$ we respectively get 20.5 and 12.4% of NH_3 in a similar way.

3. Using the data given in the initial conditions and the solution of Example 4 (p. 247), find the influence of an excess amount of hydrogen on the course of the reaction of synthesis of methanol. Perform the calculations for $[\text{H}_2]:[\text{CO}] = 3:1$, $4:1$ and $5:1$.

Solution. We denote by m the number of moles of H_2 per mole of CO . Now Eq. (10.1), in accordance with the data found in solving the example indicated above, will become

$$1.43 \times 10^{-5} = 0.434 \frac{x}{(1-x)(m-2x)^2} \left(\frac{300}{1+m-2x} \right)^{1-3}$$

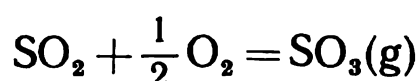
or

$$\frac{x(1+m-2x)^2}{(1-x)(m-x)^2} = 2.97$$

Consecutively inserting into this equation $m=3$, 4 and 5 , by the method of selection we find the following values of x and the content of methanol in per cent:

m	3	4	5
x	0.558	0.616	0.648
$\text{CH}_3\text{OH}, \%$	19.35	16.35	13.878

4. Show that for the reaction



the degree of oxidation in an equilibrium mixture of sulphur dioxide into sulphur trioxide is equal to

$$y = \frac{K_p p_{\text{O}_2}^{0.5}}{1 + K_p p_{\text{O}_2}^{0.5}}$$

What conclusions can be made from this equation?

Solution. From the equation

$$K_p = \frac{p_{\text{SO}_3}}{p_{\text{SO}_2} p_{\text{O}_2}^{0.5}}$$

it follows that

$$\frac{p_{\text{SO}_2}}{p_{\text{SO}_3}} = \frac{1}{K_p p_{\text{O}_2}^{0.5}} \quad \text{and} \quad \frac{p_{\text{SO}_2}}{p_{\text{SO}_3}} + 1 = \frac{1}{K_p p_{\text{O}_2}^{0.5}} + 1$$

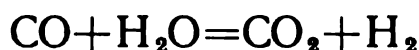
whence we get the sought equation

$$\frac{p_{\text{SO}_2} + p_{\text{SO}_3}}{p_{\text{SO}_2}} = \frac{1 + K_p p_{\text{O}_2}^{0.5}}{K_p p_{\text{O}_2}^{0.5}}$$

It follows from the equation found that the yield of sulphur trioxide depends to a greater extent on the oxygen content in the equilibrium mixture at a higher temperature (since with a growth in the temperature the equilibrium constant diminishes). At a low temperature, when $K_p \gg n_{\text{O}_2}$, the quantity y tends to unity regardless of the value of p_{O_2} .

Therefore, if, for example, we conduct the process in two steps—at 575 and at 450°C and use coal pyrites (which results in a decrease in the content of O_2), then at 450°C, even with a great coal content, the yield of sulphur trioxide will diminish insignificantly (at 8% of C by 0.8%). At 575°C the yield lowers appreciably (at 8% of C by 5.4%).

5. Show on the example of the reaction



that the maximum concentration of the products will be obtained at the stoichiometric ratio between the reactants.

Solution. Assume that in one mole of an equilibrium mixture, the mole fractions of carbon monoxide, water vapour (steam), carbon dioxide, hydrogen and an inert gas are respectively x_{CO} , $x_{\text{H}_2\text{O}}$, x_{CO_2} , x_{H_2} , and x_{in} . Let us introduce the notation

$$\frac{x_{\text{H}_2\text{O}}}{x_{\text{CO}}} = r$$

Hence

$$\frac{x_{\text{H}_2\text{O}}}{r} + x_{\text{H}_2\text{O}} = 1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}}$$

whence

$$x_{\text{H}_2\text{O}} + r x_{\text{H}_2\text{O}} = r (1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}})$$

Consequently

$$x_{\text{H}_2\text{O}} = \frac{r}{1+r} (1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}})$$

and

$$x_{\text{CO}} = \frac{1}{1+r} (1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}})$$

On the basis of the found values of x_i , the equilibrium constant of the reaction considered above is equal to

$$K = \frac{x_{\text{CO}_2} x_{\text{H}_2} (1+r)^2}{(1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}})^2 r}$$

or

$$y = \frac{r}{(1+r)^2} = \frac{x_{\text{CO}_2} x_{\text{H}_2}}{(1 - x_{\text{CO}_2} - x_{\text{H}_2} - x_{\text{in}})^2 K}$$

and

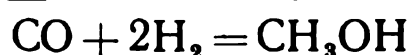
$$\frac{\partial y}{\partial r} = \frac{(1+r)^2 - 2r(1+r)}{(1+r)^4} = \frac{1-r}{(1+r)^3}$$

Equating the derivative to zero, we find that $r=1$. Since

$$\frac{\partial^2 y}{\partial r^2} = \frac{(1+r)^3 - (1-r) \cdot 3(1+r)^2}{(1+r)^6} < 0$$

then at $r=1$ the yield of the products will be maximum.

6. If we assume that $\sum n=1$ and $K_p=1$, then for the reaction



we have

$$\frac{4K_p p^2}{3^3} = \frac{x}{\left[1 - x - \frac{i}{1 - 3Mlx/A}\right]^3} \quad (\text{a})$$

and

$$C = 1.43Mlx \quad (\text{b})$$

where x = fraction of methanol in an equilibrium mixture

A = volume of the newly supplied gas, m^3

M = volume of the circulating gas, m^3

i = fraction of an inert gas in an equilibrium mixture

l = ratio of the practical yield to the theoretical one

C = practical yield of methanol, kg.

Prove the truth of Eq. (a). Consider that the content of inert gases in the reaction gas and in the products of interaction is the same (this assumption leads to an insignificant error, since the actual content of the methanol in the reaction mixture is several per cent).

Solution. We denote the fraction of the inert gas by d . Hence

$$p_{\text{CH}_3\text{OH}} = xp; \quad p_{\text{H}_2} = \frac{2}{3}(1-x-d)p;$$

$$p_{\text{CO}} = \frac{1}{3}(1-x-d)p \quad \text{and} \quad p_{\text{in}} = dp$$

$$K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}} p_{\text{H}_2}^2} = \frac{xp}{\frac{1}{3}(1-x-d)p \frac{2^2}{3^2}(1-x-d)^2 p^2} = \frac{3^3 x}{4(1-x-d)^3 p^2}$$

or

$$\frac{4K_p p^2}{3^3} = \frac{x}{(1-x-d)^3} \quad (\text{c})$$

Since one molecule is produced from three, then $\frac{3 \times 22.4}{32.0} C = 2.1C \text{ m}^3$ of the mixture is used up per mole of methanol.

The amount of gas discharged from the system will be $A - 2.1C$ m³. The balance of the inert gas will be

$$Ai = (A - 2.1C) d \text{ or } d = \frac{A}{A - 2.1C}$$

Since 1 m³ of methanol weighs $32.0/22.4 = 1.43$ kg, we get

$$C = 1.43Mlx$$

i.e. Eq. (b). Consequently, the fraction of the inert gas in the mixture is

$$d = \frac{Ai}{A - 2.1 \times 1.43Mlx} = \frac{i}{1 - 3Mlx/A}$$

Inserting this value in Eq. (c), we get Eq. (a).

7. For the reaction



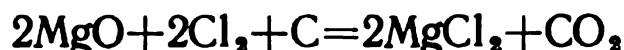
we have $\Delta G_{1000}^\circ = 4610$ cal/mol. Is the formation of methane at 1000 K and 1 atm possible if the gas contacting the carbon consists of 10% of CH₄, 80% of H₂ and 10% of N₂?

Solution. In accordance with Eq. (10.4) we have

$$\begin{aligned} \Delta G &= RT \ln \frac{p_{CH_4}}{p_{H_2}^2} + \Delta G^\circ = 4.576 \times 1000 \log \frac{0.1}{0.8^2} + 4610 = \\ &= -3690 + 4610 = 920 \text{ cal/mol} \end{aligned}$$

Since $\Delta G > 0$, the reaction is impossible—cracking of the methane will occur.

8. It was established that the reaction



proceeds at a temperature of 200–300 °C in the direction of formation of anhydrous magnesium chloride.

Substantiate this fact thermodynamically with the aid of the following data:

Substance	MgO	Cl ₂	C	MgCl ₂	CO ₂
ΔH_{298}° , cal/mol	−146 100	0	0	−153 300	−94 030
ΔS_{298}° , cal/mol · K	6.55	53.31	1.40	21.4	51.08

Solution. For the above reaction we have

$$\begin{aligned} \Delta H_{298}^\circ &= 2(-153\,300) + (-94\,030) - 2(-146\,100) = \\ &= -108\,430 \text{ cal/mol} \\ \Delta S_{298}^\circ &= 2 \times 21.4 + 51.08 - 2 \times 6.55 - 2 \times 53.31 - 1.40 = \\ &= -27.24 \text{ cal/mol} \cdot K \end{aligned}$$

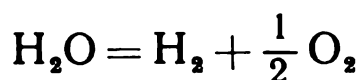
Therefore by Eq. (9.19) we have

$$\Delta G_{298}^{\circ} = -108\,430 - 298.2(-27.24) = -100\,310 \text{ cal/mol}$$

Notwithstanding the fact that the found value relates to standard conditions (during the entire process $p_{\text{Cl}_2} = 1 \text{ atm}$ and $p_{\text{CO}_2} = 1 \text{ atm}$), it is very small. For this reason it may be considered that the reaction is possible in practically any conditions. The calculations have been performed for $t = 25^{\circ}\text{C}$, but this is also not significant, since the temperature interval is not great (about 250°C), and although the reaction is exothermal, ΔG° at $t = 200$ to 300°C will only slightly differ from ΔG_{298}° .

Problems

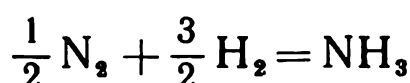
1. For the reaction



we have $\log(K)_{2400} = -2.41$.

Up to what value does the pressure have to be raised for the degree of dissociation of the steam to be halved if initially $p = 0.5$?

2. Find the influence of the pressure on the reaction of synthesis of ammonia



if the mixture fed into the synthesis column consists of 25% of N_2 and 75% of H_2 and the temperature is maintained at 750 K . Use a chart of $K_p = f(p, T)$ (Fig. 62) and the results of solving Problem 8 on p. 250 for the calculations.

Perform the calculations for every 200 atm within the range from 100 to 900 atm.

What conclusions can be made from a comparison of the results of solving the present problem and Example 2?

3. Show that the fraction of the newly formed ammonia in a mixture is

$$x_{\text{NH}_3} = \frac{x''_{\text{NH}_3} - x'_{\text{NH}_3}}{1 + x'_{\text{NH}_3}} \quad (\text{a})$$

and the fraction of the inert gas is

$$x''_{\text{in}} = \frac{x'_{\text{in}} (1 + x''_{\text{NH}_3})}{1 + x'_{\text{NH}_3}} \quad (\text{b})$$

while the concentrations of the hydrogen and nitrogen are

$$x''_{\text{H}_2} = \frac{x'_{\text{H}_2} (1 + x''_{\text{NH}_3}) - 1.5 (x''_{\text{NH}_3} - x'_{\text{NH}_3})}{1 + x'_{\text{NH}_3}}$$

and

$$x_{N_2}'' = \frac{x_{H_2}'(1 + x_{NH_3}'') - 0.5(x_{NH_3}'' - x_{NH_3}')}{1 + x_{NH_3}'} \tag{c}$$

In these equations the superscripts (') and (") relate to the initial and final compositions of the mixture, respectively.

4. The gas fed into a synthesis column has the following composition (%): H₂—70, N₂—24.5, NH₃—3.5 and CH₄—2. After the reaction, the mixture contains 17% of NH₃.

Using the equation derived in solving Problem 3, find: (1) the content (%) of newly formed ammonia; (2) the increase in the content of inert gas; (3) the change in the ratio [H₂]:[N₂]. How would it be possible to increase the ratio [H₂]:[N₂]?

5. On the basis of the results obtained in solving Problem 1 determine what amount of hydrogen has to be added to 1 mole of vapour for the degree of dissociation to lower to 0.015 at *p*=0.5 atm.

6. According to the results of solving Example 3 on p. 246, determine the possibility of reaching the yield of sulphur trioxide indicated in it if the gas contains 7% of SO₂ and 11% of O₂.

7. Semi-water gas consisting of 34% of carbon monoxide, 36% of hydrogen, 7% of carbon dioxide and 23% of nitrogen with methane is subjected to conversion at *p*=1 atm and *T*=800 K.

Find the consumption of steam ensuring the conversion of the carbon monoxide by 94% if (*K_p*)₈₀₀=4.038.

8. Determine the equilibrium concentration of methanol with the aid of the equation found in solving Example 6 if for *t*=390 °C and *p*=300 atm we have *K*=1.43×10⁻⁶, *K_v*=0.434, *i*=0.1, *l*=0.50 and *M/A*=5.

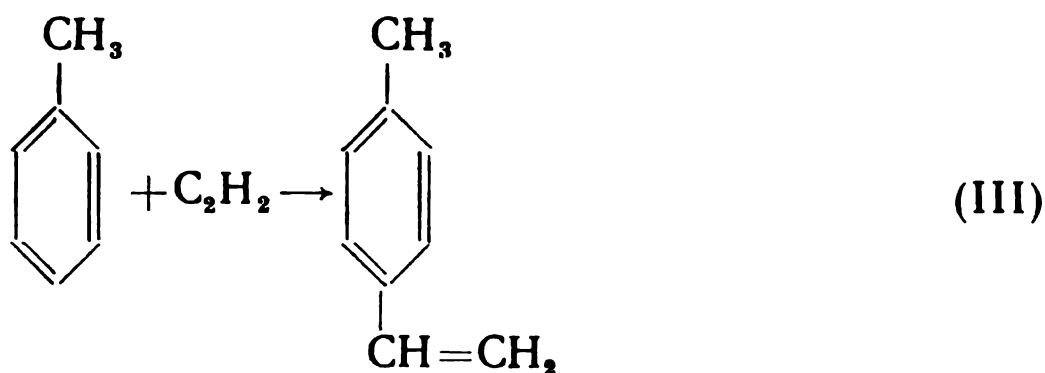
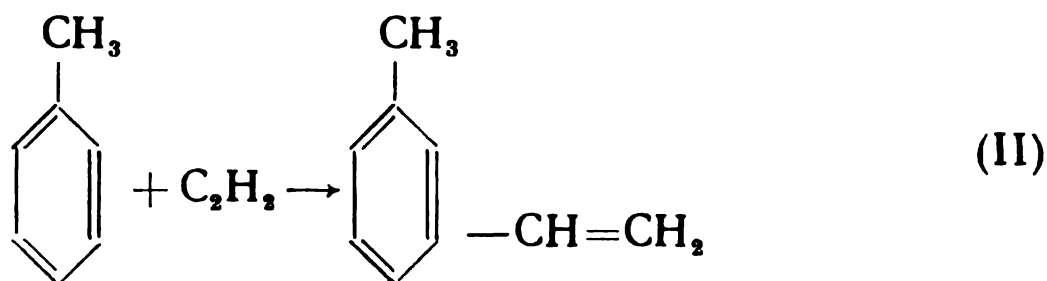
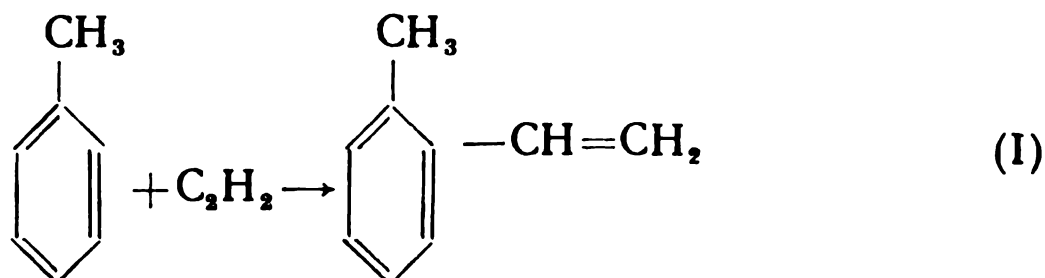
Compare the result with that obtained in solving Problem 9 of Sec. 10.1 (p. 250).

9. Determine the pressure needed to accomplish the reaction of synthesis of methane in the conditions of Example 7.

Table 24

<i>T</i>	log <i>K_p</i> for reactions:		
	(I)	(II)	(III)
600	6.6136	7.1746	6.9416
700	4.6526	5.1776	4.9336
800	3.1726	3.6696	3.4186
900	2.0223	2.4993	2.2413

10. In the alkylation of toluene with acetylene the following methyl styrenes are formed:



On the basis of the values of $\log K_p$ for reactions (I), (II) and (III) given in Table 24, determine the degree of conversion of acetylene according to these reactions at $T=600, 700$ and 900 K and at $p=1$ atm, assuming the initial ratio of [toluene]:[acetylene]=1:1.

1. Up to what temperature do these reactions proceed practically to the end?

2. How does an increase in pressure affect this temperature?

3. What will be the form of the equation showing the pressure dependence of the yield of methyl styrene if the initial mixture contains m moles of C_7H_8 and n moles of C_2H_2 ?

11. Will the direction of the reaction considered in Example 7 change if the content of nitrogen in the originally taken mixture with a constant ratio of hydrogen to methane grows to 55%?

12. The equation

$$\log K = \frac{9620}{T} - 18.041$$

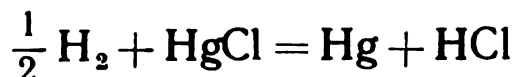
was proposed as a result of studying the reaction



within the temperature interval from 232 to 292°C .

Find the temperature at which this reaction is possible if $p=1$ atm and the initial gas mixture consists of 10% of ethylbenzene, 50% of hydrogen and 40% of ethylcyclohexane.

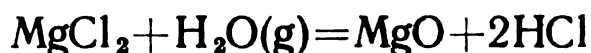
13. The reaction



proceeds in a galvanic cell.

Determine the direction of the reaction and compute ΔG_{298}° if at $t=25^\circ\text{C}$, $p_{\text{H}_2}=0.9$ and $p_{\text{HCl}}=0.01$ atm the e.m.f. is 0.011 V.

14. Tell whether it is possible to obtain HCl by the reaction



if

$$(\Delta G_{298}^\circ)_{\text{MgCl}_2} = -141\,500 \text{ cal/mol}, (\Delta G_{298}^\circ)_{\text{H}_2\text{O}} = -54\,635 \text{ cal/mol},$$

$$(\Delta G_{298}^\circ)_{\text{MgO}} = -136\,400 \text{ cal/mol} \text{ and } (\Delta G_{298}^\circ)_{\text{HCl}} = -22\,740 \text{ cal/mol}$$

10.3. CALCULATING THE EQUILIBRIUM OF COMPLEX PROCESSES

The equilibrium of complex processes (simultaneously proceeding reactions) is calculated by the simultaneous solution of equations determining the equilibrium constants for all the reactions. To simplify the calculations, it is first necessary to exclude the reactions for which the equilibrium constants are either very small or very great.

Examples

1. Determine the composition of an equilibrium mixture at 800 K in the process of isomerization of normal pentane. Take into consideration the possibility of proceeding of the reactions



Assume that at 800 K we have $\Delta G^\circ=58\,770$ cal/mol for C_5H_{12} , $\Delta G^\circ=57\,840$ cal/mol for $\text{iso-C}_5\text{H}_{12}$ and $\Delta G^\circ=61\,930$ cal/mol for $\text{C}(\text{CH}_3)_4$.

Solution. In accordance with the values of ΔG° given above we find

$$\Delta G_{\text{I}}^\circ = 57\,840 - 58\,770 = -930 \text{ cal/mol and}$$

$$\Delta G_{\text{II}}^\circ = 61\,930 - 58\,770 = 3160 \text{ cal/mol}$$

whence

$$\log K_{\text{I}} = - \frac{-930}{4.576 \times 800} = 0.254 \quad \text{and} \quad K_{\text{I}} = 1.795$$

$$\log K_{\text{II}} = - \frac{3160}{4.576 \times 800} = -0.8632 \quad \text{and} \quad K_{\text{II}} = 0.137$$

We shall proceed from one mole of an equilibrium mixture which consists of x moles of *iso*-pentane, y moles of neopentane and $(1-x-y)$ moles of pentane. Hence

$$K_I = \frac{p_{iso-C_5H_{12}}}{p_{C_5H_{12}}} = \frac{xp}{(1-x-y)p} \quad (a)$$

$$\frac{x}{1-x-y} = 1.795$$

and

$$K_{II} = \frac{py}{(1-x-y)p} \quad (b)$$

$$\frac{y}{1-x-y} = 0.137$$

The simultaneous equations obtained can be solved in an ordinary way. For simplification of the calculations, however, the following notation is introduced:

$$x+y=u \text{ and } 1-x-y=1-u$$

Now Eqs. (a) and (b) become

$$K_I = \frac{x}{1-u}; \quad K_{II} = \frac{y}{1-u}$$

or

$$K_I(1-u) = x \quad (c)$$

$$K_{II}(1-u) = y \quad (d)$$

whence

$$(K_{II} + K_I)(1-u) = x + y \quad \text{and} \quad u = \frac{K_I + K_{II}}{K_I + K_{II} + 1}$$

In the conditions of the present example

$$u = \frac{1.795 + 0.137}{1.795 + 0.137 + 1} = \frac{1.932}{2.932} = 0.659$$

and in accordance with Eqs. (c) and (d) we have

$$x = 1.795(1-0.659) = 0.612 \quad \text{and} \quad y = 0.137(1-0.659) = 0.0467$$

Consequently, the equilibrium mixture will contain 61.2% of *iso*-pentane, 4.7% of neopentane and 34.1% of pentane.

2. Find the equilibrium composition of the gas mixture formed as a result of the conversion of methane with steam at 900 K, 1 atm and $[H_2O]:[CH_4]=4:1$. In solving the problem, determine the possibility

of proceeding of the following reactions:



Use the following data for the calculations:

Reaction	I	II	III	IV	V	VI	VII
K_p . .	1.306	2.879	3.077	2.356	2.204	5.192	1.080×10^{-23}
Reaction	VIII		IX			X	
K_p . .	7.491×10^{-12}		1.442×10^{-12}			3.180×10^{-12}	

Consider that no carbon is liberated when there is an excess amount of steam.

Solution. The calculations are simplified, firstly, because of ten reactions four are independent ones, secondly, for reactions (VII-X) the equilibrium constants are so small that these reactions proceed to a negligible extent. Reactions (III), (IV) and (VI) are excluded in view of the initial conditions (carbon is liberated in them). Thus, the entire calculations can be reduced to computation of the equilibrium of the reactions



Let us denote by x the number of moles of CH_4 that have reacted according to Eq. (I), and by y the number of moles of CO reacted according to Eq. (V). Hence

$$n_{\text{CH}_4} = 1 - x$$

$$n_{\text{CO}_2} = y$$

$$n_{\text{H}_2\text{O}} = 4 - x - y$$

$$n_{\text{H}_2} = 3x + y$$

$$n_{\text{CO}} = x - y$$

$$\sum n_i = 5 + 2x$$

By Eq. (10.1) we have

$$K_1 = 1.306 = \frac{(x-y)(3x+y)^3}{(1-x)(4-x-y)(5+2x)^2}$$

(a)

and

$$K_v = 2.204 = \frac{y(3x+y)}{(x-y)(4-x-y)}$$

(b)

We perform the calculations by the method of selection:

Assumed value of x	0.9	0.95	0.92
Value of y from Eq. (b)	0.5677	0.5826	0.5735
Right-hand part of Eq. (a)	0.990	2.530	1.368

By interpolation we find $x \approx 0.938$ and $y \approx 0.579$. Consequently, an equilibrium mixture will contain

$$\begin{aligned} 1 - 0.938 &= 0.062 \text{ mol} = 0.90\% \text{ of } \text{CH}_4 \\ &\quad 0.579 \text{ mol} = 8.42\% \text{ of } \text{CO}_2 \\ 4 - 0.938 - 0.579 &= 2.483 \text{ mol} = 36.11\% \text{ of } \text{H}_2\text{O} \\ 3 \times 0.938 + 0.579 &= 3.393 \text{ mol} = 49.35\% \text{ of } \text{H}_2 \\ 0.938 - 0.579 &= 0.359 \text{ mol} = 5.22\% \text{ of } \text{CO} \end{aligned}$$

$$\text{Total} = 6.876 \text{ mol}$$

3. Discuss the possibility of nitrogen fixation at $T = 2000$ and 3500 K according to the reaction



Is it possible to neglect the dissociation of hydrogen



which lowers the degree of utilization of the nitrogen?
Use the following data for the calculations (Table 25).

Table 25

Substance	S_{298}°	ΔH_{298}°	C_p
N ₂	45.79	0	$6.65 + 1.00 \times 10^{-3}T$
H ₂	31.23	0	$6.65 + 0.69 \times 10^{-3}T$
C	1.40	0	$2.673 + 2.617 \times 10^{-3}T - \frac{1.169 \times 10^5}{T^2}$
HCN	48.23	30 900	$10.13 + 2.08 \times 10^{-3}T - \frac{2.49 \times 10^5}{T^2}$
H	27.40	51 900	4.97

Solution. Let us find the equation showing the temperature dependence of the equilibrium constant for reaction (I):

$$\Delta G_{298}^{\circ} = 30\,900 - 298.2(48.23 - 0.5 \times 45.79 - 0.5 \times 31.23 - 1.40) = 30\,900 - 2481 = 28\,419 \text{ cal/mol}$$

$$\Delta a = 10.13 - (0.5 \times 6.65 + 0.5 \times 6.65 + 2.673) = 0.807$$

$$\Delta b = [2.08 - (0.5 \times 1.00 + 0.5 \times 0.69 + 2.617)] \times 10^{-3} = -1.382 \times 10^{-3}$$

$$\Delta c' = [(-2.49) - (-1.169)] \times 10^5 = -1.321 \times 10^5$$

Therefore in accordance with Eq. (2.24)

$$30\,900 = \Delta H_0^{\circ} + 0.807 \times 298.2 - 0.691 \times 10^{-3} \times 298.2^2 + \frac{1.321 \times 10^5}{298.2}$$

whence

$$\Delta H_0^{\circ} = 30\,900 - 240.6 + 61.5 - 443 = 30\,278 \text{ cal/mol}$$

By Eq. (9.7)

$$28\,419 = 30\,278 - 0.807 \times 298.2 \times 2.303 \times 2.47\,451 + 0.691 \times 10^{-3} \times 298.2^2 - \frac{0.6605 \times 10^5}{298.2^2} + 298.2/I$$

whence

$$I = \frac{28\,419 - 30\,278 + 1371 - 61.5 + 0.7}{298.2} = -\frac{548.8}{298.2} = -1.84$$

After inserting the values obtained into Eq. (9.6), the equation sought becomes

$$\log K_1 = -\frac{30\,278}{4.576T} + \frac{0.807}{1.987} \log T - \frac{1.382 \times 10^{-3}}{9.150} T + \frac{1.321 \times 10^5}{9.150T^2} + \frac{1.84}{4.576}$$

or

$$\log K_1 = -\frac{6\,617}{T} + 0.406 \log T - 0.000\,151T + \frac{14\,437}{T^2} + 0.4022$$

We find the equation showing the temperature dependence of the equilibrium constant for reaction (II):

$$\Delta G_{298}^{\circ} = 103\,800 - 298.2(2 \times 27.40 - 31.23) = 96\,770 \text{ cal/mol}$$

According to Eq. (2.24)

$$103\,800 = \Delta H_0^{\circ} + 3.29 \times 298.2 - 0.345 \times 10^{-3} \times 298.2^2$$

whence

$$\Delta H_0^{\circ} = 103\,800 - 981 + 31 = 102\,850 \text{ cal/mol}$$

By Eq. (9.7)

$$96\,770 = 102\,850 - 3.29 \times 298.2 \times 2.303 \times 2.47\,451 + 0.345 \times 10^{-3} \times 298.2^2 + 298.2/I$$

whence

$$I = \frac{96\,770 - 102\,850 + 5591 - 31}{298.2} = \frac{-520}{298.2} = -1.744$$

In accordance with Eq. (9.6), the equation sought has the form

$$\log K_{II} = -\frac{103\,800}{4.576T} + \frac{3.29}{1.987} \log T - \frac{0.345 \times 10^{-3}}{9.150} T + \frac{1.744}{4.576}$$

or

$$\log K_{II} = -\frac{22\,684}{T} + 1.656 \log T - 0.000\,037\,7T + 0.3812$$

We calculate the equilibrium constants according to the found equations of the temperature dependence of $\log K$. For $T=2000$ K we have

$$\begin{aligned} \log K_I &= -\frac{6617}{2000} + 0.406 \times 3.301\,03 - 0.000\,151 \times 2000 + \frac{14\,437}{2000^2} + \\ &+ 0.4022 = -3.3085 + 1.340 - 0.302 + 0.004 + 0.4022 = \\ &= -1.8643 = \bar{2}.1357 \end{aligned}$$

and $K_I = 0.0137$.

$$\begin{aligned} \log K_{II} &= -\frac{22\,684}{2000} + 1.656 \times 3.301\,03 - 0.000\,037\,7 \times 2000 + 0.3812 = \\ &= -11.342 + 5.466 - 0.0754 + 0.3812 = -5.5702 = \bar{6}.4298 \end{aligned}$$

whence $K_{II} = 2.69 \times 10^{-6}$.

It follows from the data obtained that at $T=2000$ K the dissociation of the hydrogen may be left out of account.

We find the yield of HCN:

$$K_I = \frac{x}{(0.5 - 0.5x)^{0.5} (0.5 - 0.5x)^{0.5}} \quad \text{or} \quad 0.0137 = \frac{x}{0.5 - 0.5x}$$

whence

$$0.0068 - 0.0068x = x \quad \text{and} \quad x = \frac{0.0068}{1.0068} = 0.006\,75 \approx 0.7\% \text{ of HCN}$$

We perform the calculations for $T=3500$ K:

$$\begin{aligned} \log K_I &= -\frac{6617}{3500} + 0.406 \log 3500 - 0.000\,151 \times 3500 + \\ &+ \frac{14\,437}{3500^2} + 0.4022 = -1.890 + 1.439 - 0.5285 + \\ &+ 0.0012 + 0.4022 = -0.5771 = \bar{1}.4229 \end{aligned}$$

and $K_I = 0.265$.

Therefore

$$0.265 = \frac{x}{0.5 - 0.5x} \quad \text{and} \quad x = \frac{0.1325}{1.1325} = 0.117 = 11.7\%$$

$$\begin{aligned} \log K_{II} &= -\frac{22\,684}{3500} + 1.656 \log 3500 - 0.000\,037\,7 \times 3500 + 0.3812 = \\ &= -6.481 + 5.869 - 0.1320 + 0.3812 = -0.3628 = \bar{1}.6372 \end{aligned}$$

and $K_{II} = 0.434$.

Since

$$K_{II} = \frac{(2x)^2}{1-x} \left(\frac{p}{1+x} \right)^{2-1} = \frac{4x^2}{1-x^2}$$

then

$$0.434 = \frac{4x^2}{1-x^2} \quad \text{and} \quad 0.434 - 0.434x^2 = 4x^2$$

whence

$$x = \sqrt{\frac{0.434}{4.434}} = 0.313$$

Consequently,

$$\frac{2 \times 0.313}{1 + 0.313} \times 100 = \frac{62.6}{1.313} = 47.7\% \text{ of H}$$

The result shows that at 3500 K the dissociation of the hydrogen may not be neglected. Let us denote by x the number of moles of N_2 reacting in accordance with Eq. (I), and by y the number of moles of H_2 reacting in accordance with Eq. (II). For an equilibrium mixture we thus obtain

$$\begin{aligned} n_{N_2} &= 0.5 - x \\ n_{H_2} &= 0.5 - x - y \\ n_{HCN} &= 2x \\ n_H &= 2y \\ \hline \sum n_i &= 1 + y \end{aligned}$$

Consequently,

$$0.265 = \frac{2x}{\sqrt{0.5-x} \sqrt{0.5-x-y}}$$

and

$$0.434 = \frac{4y^2}{(0.5-y-x)(1+y)}$$

By the method of selection we find $x \approx 0.04$ and $y \approx 0.187$, i.e. an equilibrium mixture contains (in per cent): N_2 —38.8, H_2 —23.0, HCN—6.7 and H—31.5.

Problems

1. The following reactions proceed in the process of preparation of air-producer gas:



The temperature dependence of K_I and K_{II} can be represented by the following approximate equations:

$$\log K_I = \frac{20\,600}{T} + 0.153$$

and

$$\log K_{II} = \frac{5794}{T} + 4.680$$

On the basis of the values of the equilibrium constants at $T=600, 800, 1000$ and 1200 K make conclusions on the course of the process being considered.

2. The process of isomerization of normal heptane can proceed in the following directions:

- $n\text{-heptane} = 2\text{-methyl-hexane}$ (I)
- $n\text{-heptane} = 3\text{-methyl-hexane}$ (II)
- $n\text{-heptane} = 3\text{-ethyl-pentane}$ (III)
- $n\text{-heptane} = 2,2\text{-dimethyl-pentane}$ (IV)
- $n\text{-heptane} = 2,3\text{-dimethyl-pentane}$ (V)
- $n\text{-heptane} = 2,4\text{-dimethyl-pentane}$ (VI)
- $n\text{-heptane} = 3,3\text{-dimethyl-pentane}$ (VII)
- $n\text{-heptane} = 2,2,3\text{-trimethyl-butane}$ (VIII)

The following equilibrium constants of these reactions were found on the basis of spectroscopic data:

T	400	600	800	T	400	600	800
K_I	3.68	1.77	1.24	K_V	9.57	2.88	1.55
K_{II}	3.87	2.36	1.85	K_{VI}	2.46	0.60	0.30
K_{III}	0.40	0.29	0.25	K_{VII}	3.16	0.80	0.43
K_{IV}	4.73	0.74	0.31	K_{VIII}	2.09	0.38	0.17

Calculate the composition of an equilibrium mixture and make the relevant conclusions from the data obtained.

3. On the basis of the results of solving Example 2, check the truth of the assumption on which these calculations are based that it is impossible to liberate carbon.

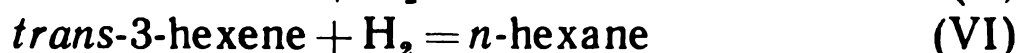
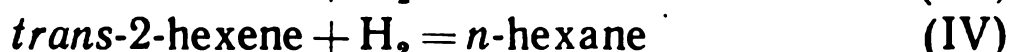
4. The equation

$$\log K_p = \frac{6366}{T} - 2.961 \log T + 0.0007668T - 0.0000001764T^2 + 0.11 \quad (\text{a})$$

was proposed for the reaction of hydrogenation of hexenes ($p=1$ atm, $t=350$ to 450°C)



The following reactions may proceed in the given process:



1. Show that the following relationship exists between the equilibrium constants of reactions (I-VI):

$$\frac{1}{K_I} = \sum_{\text{II}}^{\text{VI}} \frac{1}{K_i}$$

2. Use this relationship to calculate the values of $\log K_p$ for $T=600$, 700 and 800 K; compare the results obtained with experimental data. The Gibbs energies of formation of the reactants are given in Table 26.

Table 26

$T, \text{ K}$	ΔG_T°					
	$n\text{-C}_6\text{H}_{14}$	$1\text{-C}_6\text{H}_{12}$	$cis\text{-2-C}_6\text{H}_{12}$	$trans\text{-2-C}_6\text{H}_{12}$	$cis\text{-3-C}_6\text{H}_{12}$	$trans\text{-3-C}_6\text{H}_{12}$
600	43.02	54.57	52.7	52.5	53.7	53.3
700	57.98	66.25	64.5	64.3	65.7	65.2
800	73.08	78.02	76.4	76.3	77.7	77.3

5. Considering that upon the conversion of methane with carbon dioxide in the presence of carbon, the following reactions should be taken into account:



and



Determine the composition of an equilibrium mixture at $t=700$ and 900°C at $[\text{CO}_2]:[\text{CH}_4]=1:1$ and $5:1$ and the pressure $p=1$ and 20 atm.

Use the following data for the calculations:

for $t=700^\circ\text{C}$

$$(K_p)_I = 12.95, \quad (K_p)_{II} = 0.64 \quad \text{and} \quad (K_p)_{III} = 0.915$$

for $t=900^\circ\text{C}$

$$(K_p)_I = 2451.7, \quad (K_p)_{II} = 1.35 \quad \text{and} \quad (K_p)_{III} = 36.5$$

Perform the same calculations for conversion in the absence of carbon.

Use the results obtained to reach a conclusion on the influence of the temperature, the ratio $[\text{CO}_2]:[\text{CH}_4]$ and the pressure on the composition of the conversion products.

ANSWERS TO PROBLEMS *

Chapter One

2. $W = -596$ cal; $W_2 - W_1 = 236$ cal.
3. $t = 24^\circ\text{C}$.
4. $W = -2920$ cal.
5. $\Delta U = 457.9$ kcal/kg.
6. (1) $W = 47\,000$ atm·cm³; (2) no, since the discrepancy (23%) is much greater than the error of the experimental data.
7. $W = -529\,500$ kg·m/m³ = 1.44 kWh/m³ = 1.93 hp·h/m³ = 687 kWh/m³ of O₂.
8. Yes, they can.
9. $Q = 42.8$ kcal.
10. $Q_V = 781\,100$ cal/mol.

Chapter Two

SECTION 2.1

1. $\Delta H = 10.519$ kcal/mol.
2. $\Delta H = -11.21$ kcal/mol.
3. $\Delta H = -22.03$ kcal/mol.
4. $\Delta H = -73.3$ kcal/mol.
5. $\Delta H = -189.60$ kcal/mol; $\Delta H = -153.3$ kcal/mol.
6. $\Delta H = -483.2$ kcal/mol.
7. No, since the difference between Q_p and Q_V (0.546 kcal/mol) is beyond the limits of the accuracy for the values of the heats of combustion of C and CO.
8. $\Delta H = -2.80$; the coincidence is within the limits of the accuracy of experiment.
9. 0.184; -29.83; -30.037 kcal/mol.
10. $\Delta H = -820.3$ kcal/mol.
11. $\Delta H = -14.179$ kcal/mol (0.6%).
12. $\Delta H = -114.89$, -39.65 and -99.73 kcal/mol.
13. $\Delta H = 13.51$ kcal/mol (0.24 kcal/mol, 1.75%).

* The figures in parentheses show the discrepancy between the calculated values and those indicated in the initial conditions of the problem.

14. (1) $\Delta H = 6.57$ kcal/mol; (2) $\Delta H = 12.13$ kcal/mol; (3) $\Delta H = 18.70$ kcal/mol.
15. $\Delta H \approx 0.67$ kcal.
16. $\Delta H = 1.17$ kcal/mol.
17. $\Delta H = 0.45$ kcal/mol.
18. $\Delta H = -2.39$ kcal/mol.
19. $\Delta H = -188.84$ kcal/mol (4.91 kcal/mol, 2.5%).
20. $\Delta H = -54.300$ kcal/mol.
21. $\Delta H = -99.58$ kcal/mol (0.13 kcal/mol, 0.13%).
22. $\Delta H = -24.6$ kcal/mol.
23. (1) $\Delta H = 12.49$ kcal/mol; (2) $\Delta H = -337.23$ kcal/mol.
24. $\Delta H = -30.73$ kcal/mol (0.39 kcal/mol, 1.3%).
25. 2.9:1.0.
26. 30 130 kcal.
27. (1) 2.83:1; (2) 3.11:1.

SECTION 2.2

1. $\Delta H = -18.6$ kcal/mol (8.1%).
2. $\Delta H = 203.1$ kcal/mol (1.2%).
3. $\Delta H = -117.6$ kcal/mol (4.4%).
4. $\Delta H = 44.38$ kcal/mol (3.38%), -51.48 kcal/mol (1.25%).
5. $\Delta H = -103.6$ kcal/mol (0%).
6. $\Delta H = -530$ kcal/mol (0.11%).
7. $\Delta H = -537.5$ kcal/mol (0.2%).
8. $\Delta H = -1232.8$ kcal/mol.

SECTION 2.3

1. 246 kcal.
2. No, since the discrepancy (about 9%) is beyond the limits of the errors of experiment.
3. $C_p = 17.66 + 2.40 \times 10^{-3}T - 5.16 \times 10^{-5}T^{-2}$, $(C_p)_{500} = 16.80$ cal/mol \cdot K (1.1%).
4. $C_p = 20.0$ cal/mol \cdot K.
5. $C_p = 9.255 + 12.95 \times 10^{-3}T$.
6. $H_{2000} - H_{500} = 12\,100$ cal/mol.
7. $H_{1173} - H_{873} = 26\,875$ cal/mol.
8. $H_T - H_{273} = 8.63T + 0.13 \times 10^{-3}T^2 + 0.84 \times 10^5 T^{-1} - 2675$;
 $H_{1000} - H_{273} = 6170$ cal/mol.
9. (1) $H_T - H_{298} = 8.18T + 0.356 \times 10^{-3}T^2 + 0.66 \times 10^5 T^{-1} - 2692$;
 $C_p = 8.18 + 0.712 \times 10^{-3}T - 0.66 \times 10^5 T^{-2}$;
 (2) $\Delta H = 2578$ cal/mol.
10. $C_p = 7.904, 7.907$ cal/mol \cdot K (0.03%).
11. $\Delta H = 2076$ cal/mol (0.4%).

12. (1) $C_p = 8.118 \text{ cal/mol} \cdot \text{K}$ (0.38%); (2) $C_p = 8.117 \text{ cal/mol} \cdot \text{K}$ (0.39%).
 13. $C_p = 27.15 \text{ cal/mol} \cdot \text{K}$ (0.6%).
 14. (1) $C_p = 2.25 + 168.93 \times 10^{-3}T - 63.15 \times 10^{-6}T^2$; (2) $C_p = 64.58 \text{ cal/mol} \cdot \text{K}$ (0.59%).
 15. A chain structure, since for C_1 the discrepancy is 0.5%, and for C_2 and C_3 respectively 35.3 and 43.9%.
 16. $C \approx 0.39 \text{ cal/g-atom} \cdot \text{K}$ (1.5%).

SECTION 2.4

1. $t \approx 2400^\circ\text{C}$.
2. $\Delta t = -300^\circ\text{C}$.
3. $\Delta t = 140^\circ\text{C}$.
4. $t = 450^\circ\text{C}$.
5. $\Delta t = 510^\circ\text{C}$.

SECTION 2.5

1. $C_p = 7.94 \text{ cal/mol} \cdot \text{K}$ (1.9%).
2. (1) $\Delta C_p = -4.627 + 31.8 \times 10^{-3}T - 55.47 \times 10^{-6}T^2$; (2) $C_p = 6.54 \text{ cal/mol} \cdot \text{K}$ (0.3%).
3. $T \approx 1420 \text{ K}$.
4. The heat of the reaction diminishes with increasing temperature (its absolute value grows, since in the given case we have $\Delta C_p < 0$). The rate of the change in ΔH decreases, since the absolute value of ΔC_p drops.
5. $\Delta H = -10\,440 \text{ cal/mol}$.
6. $Q_v \approx -26\,306 \text{ cal/mol}$.
7. (1) $\Delta H = 41\,942 - 2.53T - 4.1915 \times 10^{-3}T + 0.525 \times 10^5 T^{-1}$;
 (2) 383.4 kcal .
8. $\Delta H = 53\,880 \text{ cal/mol}$.
9. $\Delta H = 34\,550 + 16.64T - 5.66 \times 10^{-3}T^2 + 1.26 \times 10^5 T^{-1}$;
 (a) $45\,660 \text{ cal/mol}$ (70 cal/mol, 0.15%); (b) $45\,460 \text{ cal/mol}$ (0.18%);
 (c) $47\,750 \text{ cal/mol}$ (4.7%).
10. $\Delta H = -13\,170 \text{ cal/mol}$.

Chapter Three

SECTION 3.1

7. $C_p/C_v = 1.384$.
10. about 0.006 K .
11. $\Delta T = 0.46 \text{ K}$.
12. $\Delta S = 0.537 \text{ cal/K}$.
13. $\Delta S = 29.8 \text{ cal/K}$.
14. $(\partial S/\partial V)_T = 3.36 \text{ mm Hg/K}$.

15. $(\partial S/\partial T)_p = 0.0434 \text{ cal/g} \cdot \text{K}^2$.
16. $\Delta S = 0.02325 \text{ cal/K}$.
19. $\Delta S = 42.80 \text{ cal/mol} \cdot \text{K}$.
20. $\Delta S = 0.58 \text{ cal/K}$.
21. $\Delta S = 0.038 \text{ cal/K}$.
23. $\Delta S = 19.1 \text{ cal/K}$.
24. $\Delta S = 10.67 \text{ cal/K}$.
25. $V = 2000 \text{ dm}^3$.
26. $\Delta S = 0.577 \text{ cal/K}$.
27. $\Delta S = 10.3 \text{ cal/K}$.
28. $\Delta S = -23.6 \text{ cal/mol} \cdot \text{K}$.
30. $\Delta S = 0.07 \text{ cal/K}$.
32. $\Delta S = 3.20 \text{ cal/K}$.
33. (1) $\Delta S = 1.377 \text{ cal/K}$; (2) $\Delta S = 0$; (3) $\Delta S = 0.688 \text{ cal/K}$.
34. $\Delta S \approx 15 \text{ cal/K}$.
35. $\Delta S = 0.065 \text{ cal/K}$.
36. (1) $W = 198.7 \text{ cal}$; (2) $T = 345.5 \text{ K}$.
37. $\Delta S = 0.031 \text{ cal/K}$.
38. $\Delta S = -28.3 \text{ cal/K}$.
39. $\Delta S = -25.26 \text{ cal/K}$, $W = 5820 \text{ cal}$.
40. $\Delta S = -7.71 \text{ cal/mol} \cdot \text{K}$, $S = 14.71 \text{ cal/mol} \cdot \text{K}$ (0.78 entropy units); $\Delta S = 75.79 \text{ cal/mol} \cdot \text{K}$.

SECTION 3.2

3. $(\partial \Delta G/\partial p)_T = \Delta V$. If the values of ΔG for a given process along an isotherm are known at different pressures, then upon plotting $\Delta G = f(p)$ and drawing a tangent, we get ΔV —the change in the volume in the process at the given values of p and T .

5. $\Delta A - \Delta G = 0$.
6. (1) $\Delta G = W(p_2 - p_1) + B \ln \frac{p_2 + C}{p_1 + C}$; (2) $\Delta G = 11730 \text{ cal}$.
7. $\Delta G = 20.54 \text{ cal}$.
8. (1) $\Delta G = -73.84 \text{ cal/mol}$. The process proceeds from the left to the right, i.e. benzene vapour is the stable phase; (2) $\Delta G = 0$; (3) $\Delta G = 66.88$. This process proceeds from the right to the left, i.e. liquid benzene is the stable phase.
9. $\Delta G = -27.8 \text{ cal}$, $\Delta A = 744 \text{ cal}$.
10. $W = -410.7 \text{ cal}$.
11. $\Delta G = -26110 \text{ cal/mol}$, $\Delta A = -25820 \text{ cal/mol}$.
12. $\Delta G = 20149 \text{ cal/mol}$.
13. $\Delta G_{298} \approx \Delta A_{298} = 32.3 \text{ cal/mol}$. Since $\Delta G_{298} > 0$, it follows that at $t = 25^\circ \text{C}$ rhombic sulphur will be stable.
14. $\Delta H = -2352 \text{ cal/mol}$ (0.3%).
15. $W = -689 \text{ cal}$, $\Delta U = 0$, $Q = -689 \text{ cal/mol}$, $\Delta H = 0$, $\Delta S = -1.378 \text{ cal/mol} \cdot \text{K}$, $\Delta A = -689 \text{ cal/mol}$, $\Delta G = 689 \text{ cal/mol}$.

Chapter Four

SECTION 4.1

1. By Eq. (4.1) $p=77.3$ atm (3.4%), by Eq. (4.2)—81.0 atm (1.25%), $p=91.6$ atm (14.5%).
2. The line will be a straight one.
4. $p=77.5$ atm (3.1%).
5. (1) $V_{cr}=3b$, $T_{cr}=8a/27Rb$, $p_{cr}=a/27b^2$.
6. In the equation $pV=RT+pb-a/TV+ab/TV^2$ it is necessary to neglect the last term and replace V with RT/p in the term preceding the last one.
7. $p=82.08$ atm (0.22%).
8. $Z=Z'273.2/T$.
9. $V_{H_2}=40.46$ cm³ (17.2%).
10. $Z_{cr}=0.375$, $(Z_{cr})_{av}=0.283$ (24.5%, whereas the average deviation from the experimentally found value is 4.0%).
12. (1) $p=535.4$ atm (10.8%); (2) $p=410.6$ atm (31.6%).
13. $p=197.6$ atm (1.2%).
14. $p=474$ atm (5.2%).

SECTION 4.2

1. (1) $\Delta G=773$ cal; (2) $\Delta G=1303$ cal.
2. $f=81.2$ atm (1.2%).
3. $a=2.079 \times 10^6$ (8.2%), $b=41.42$ (3.18%); $f=36.31$ atm (0.14%), 66.22 (0.42%), 91.20 (0.53%), 114.0 (1.5%) and 137.4 atm (3.6%).
4. $f=83.2$ atm (1.2%).
5. $f=116.3$ atm.
6. $f=80.1$ atm (2.6%).
7. $f=48.06$ and 42.26 atm.
8. $f=1.61$ atm; the discrepancy is far beyond the limits of the error of the equation of $p=F(t)$.
9. $f=326$ atm.

SECTION 4.3

1. It follows from the found equation that at low values of p and great ones of T we have (1) $C_p - C_v > R$; (2) the difference between C_p , C_v and R grows with the pressure approximately proportional to the latter. This difference will be greater at a lower temperature; (3) this difference is the greater, the bigger a is, i.e. the easier a gas is compressed.
2. $C_p^\circ=34.4$ cal/mol·K; the difference between C_{p-1} and C_p° (0.307) is beyond the limits of the errors of an experiment.
3. (1) $C_p=10.73$ cal/mol·K (0.5%); (2) $C_p=11.44$ cal/mol·K (5.9%).

4. $C_p - C_v = 2.47 \text{ cal/mol} \cdot \text{K}$ (5.0%).
5. $C_p = 10.76 \text{ cal/mol} \cdot \text{K}$ (0.4%).
7. No, since according to Eq. (4.4) we have $(\partial^2 V / \partial T^2)_p = 0$.
8. $C_p = 1.13 \text{ kcal/kg} \cdot \text{K}$ (5.8%).
9. $(\partial C_p / \partial p)_T = 0.010 \text{ cal/mol} \cdot \text{K} \cdot \text{atm}$.

SECTION 4.4

2. $\Delta H = 6.21 \text{ cal/mol}$. This value is about 4.6% of that given in the initial conditions, which exceeds the error of experiment, and for this reason it must be taken into account.

4. $\Delta H = 1600 \text{ cal/mol}$.
5. $\Delta H = -588 \text{ cal}$.

SECTION 4.5

1. $\mu = 0.244 \text{ K/atm}$ (2.1%).
2. $\mu = 0.179 \text{ K/atm}$ (5.9%).
4. $t_{\text{inv}} = -117.9$ and 422.5°C .
5. $\mu = 0.180 \text{ K/atm}$; (a) 6.5%; (b) 23.7%.
6. $T_{\text{inv}} = 697 \text{ K}$.
7. $\Delta t = -92^\circ \text{C}$.
8. $\Delta t = 30.3^\circ \text{C}$ (6.4%).

Chapter Five

SECTION 5.1

1. $\Delta H = 120 \text{ cal/g-atom}$.
2. $\Delta H = 4250 \text{ cal/mol}$ (7.4%).
3. The experimental data give values that agree with each other, since by the equation $T_{\text{fus}} = f(p)$ we have $(\partial T_{\text{fus}} / \partial p)_{p=1} = 0.026338$, and by Eq. (5.1) we have $(\partial T_{\text{fus}} / \partial p)_{p=1} = 0.02637$.
4. The volume of 10 kg of tin at its melting point equals 1.43 dm^3 , consequently, part of the molten tin (30 cm^3) will spill out, i.e. the crucible cannot be used for melting such an amount of the metal.
5. It is not possible to neglect the change in ΔH_{fus} with the pressure, since the discrepancy between $(\Delta H_{\text{fus}})_{p=1}$ and $(\Delta H_{\text{fus}})_{p=2500}$ is 14 cal/mol , which is probably beyond the limits of the error in the experimental data.
6. $p = 3580 \text{ atm}$. The considerable discrepancy (11.6%) is explained by the inaccuracy of the assumptions made within such a great pressure interval.
7. $\Delta H = 116.8 \text{ kcal/kg}$ (0.7%).

$$8.(1) \Delta H = 264.5 \frac{\rho T_{\text{n.b.p.}}}{T} \frac{\rho^{1q} - \rho^g}{\rho^{1q} \rho^g} \left[A - B \left(\frac{T - T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} \right) \left(\frac{T + T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} \right) \right] +$$

$$+ C \left(\frac{T - T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} \right)^2 \left(\frac{2T + T_{\text{n.b.p.}}}{T_{\text{n.b.p.}}} \right).$$

- (2) $\Delta H = 3110$ cal/mol.
9. $\Delta H = 7577, 7362, 7023, 6693, 6219, 5707, 5128, 4304, 3373, 2682, 1951$ and 1407 cal/mol.
10. At $t = 100^\circ\text{C}$: (1) 539.3 kcal/kg (0.07%); (2) 547.7 kcal/kg (1.63%); (3) 547.9 kcal/kg (1.67%).
- At $t = 369^\circ\text{C}$: (1) 248.0 kcal/kg (113%); (2) 467.1 kcal/kg (309%); (3) 550 kcal/kg (372%). Consequently, for $t = 369^\circ\text{C}$ no simplifications should be introduced into the calculations.
11. $\Delta H = 130$ cal/mol (94 cal/mol).
12. No, since ΔH_{vap} grows with the temperature.
14. $\partial p / \partial T = 19.3$ mm Hg/K (11%).
15. $\partial T / \partial p = 0.0353$ K/mm Hg (10%).
16. No, it may not, since $\partial p / \partial T = 0.0351$ differs from the exact value (see the solution of Example 2) by 1.3%, which appreciably exceeds the error in the value of ΔH_{vap} .
17. 124.1 kcal/kg.
18. (1) $t = -77.8^\circ\text{C}$, $p = 45.7$ mm Hg; (2) $\Delta H = 1380$ cal/mol (2.1%).
19. The discrepancy between the values of $\partial p / \partial T$ is 3.3%.
20. $S = 46.1$ cal/mol·K.
21. $\Delta S \approx 26$ cal/mol·K.
22. (2) $t \approx 1100^\circ\text{C}$ (20°C); (3) $p \approx 60$ mm Hg.
23. (1) $p = 83$ mm Hg and $T = 90$ K; (2) $\Delta H_{\text{subl}} = 2320$ cal/mol, $\Delta H_{\text{vap}} = 2070$ cal/mol, $\Delta H_{\text{fus}} = 250$ cal/mol.
24. $\log p = -8730/T + 7.92$, $\Delta H = 40\,000$ cal/mol.
25. $\Delta H = 273$ cal/mol (18%), $\Delta H = 218$ cal/mol (2.7%).
26. $t \approx 113^\circ\text{C}$.
27. $p = 205$ mm Hg.
28. $t = 65.4^\circ\text{C}$ (0.7°C).
29. $\Delta H = 181.8$ cal/mol.
30. $p = 66.8$ mm Hg (11.3%).
31. No, since the discrepancy between $\partial p / \partial T$ and $\Delta p / \Delta T$ is 2.2%.
32. $V = 1.823$ dm³.
33. The arithmetical mean value of $(\Delta H_{\text{vap}})_{\text{n.b.p.}} / T_{\text{n.b.p.}}$ for 15 substances equals 21.3 cal/mol·K.
34. $p \approx 343$ mm Hg (2%).
35. $t = 39^\circ\text{C}$ (0.59°C).
36. Only in the first approximation, since assuming $\Delta S_{\text{n.b.p.}} = 21$ cal/mol·K, we get $t_{\text{n.b.p.}} = 2.6^\circ\text{C}$.
37. The heating of $\text{H}_2\text{S}(\text{lq})$.

SECTION 5.2

1. p , atm . . .	5	10	20	30	40	50	60
t , $^\circ\text{C}$	114.0	139.8	169.8	189.6	204.8	217.5	228.2

The mean arithmetical discrepancy between the results of the calculations and the data given in the initial conditions is about 2.2°C ,

which is far beyond the limits of accuracy of the experimental data. This is due to the fact that the assumption which Eq. (5.5) is based on becomes untrue at high temperatures.

2. (1) $t=163.2$ (0.5 °C); (2) $p=112.5$ mm Hg (0.0%).
3. (1) $\log T_{\text{CH}_3\text{OH}}=1.016$ $\log T_{\text{H}_2\text{O}}-0.082$ 81; (2) $\Delta_{\text{av}}=0.3$ °C; $\Delta_{\text{av}}=0.6$ °C.
5. $(\Delta H_{\text{vap}})_1=C(\Delta H_{\text{vap}})_2$, where C is a constant.
6. $T_1=[(T_1)_{\text{n.b.p.}}/(T_2)_{\text{n.b.p.}}]T_2$.
7. $t=91.5$ °C (0.9%).
8. (1) $1/T_{\text{CH}_3\text{OH}}=1.121$ $(1/T_{\text{H}_2\text{O}})-0.000$ 052; (2) $\Delta_{\text{av}}=0.2$ °C; $\Delta_{\text{av}}=1.2$ °C.
9. (a) 270.1 cal/g (2.8%); (b) 270.3 cal/g (2.8%); (c) 270.5 cal/g (2.9%).
10. (a) 206.4 cal/g (46.1%); (b) 205.7 cal/g (45.6%); (c) 205.0 cal/g (45.1%).
11. The average discrepancy is 17 mm Hg.
12. $p \approx 198.6$ mm Hg.
14. $t_{\text{n.b.p.}} \approx 155$ °C, $p_{t=72} \approx 48$ mm Hg.

SECTION 5.3

1. $a=1.79 \times 10^7$, $b \approx 117.8$.
2. $p_{\text{cr}}=a/4e^2b^2$, $V_{\text{cr}}=2b$ and $T_{\text{cr}}=a/4Rb$.
3. $(\partial V/\partial p)_T=\infty$.
4. $(\rho^{\text{li}}+\rho^{\text{g}})/2=0.1583-0.002$ 28 t g/cm³.
5. $t_{\text{cr}}=239.2$ °C. The good coincidence with the value indicated in the initial conditions of the problem is due to compensation of the errors, since the value of $t_{\text{n.b.p.}}$ given in the initial conditions of the problem differs from the most authentic value by 12.6 °C (68.2 °C instead of 55.6 °C).
6. (1) $p_{\text{cr}}=48.4$ atm; (2) $p_{\text{cr}}=48.0$ atm; (3) $p_{\text{cr}}=49.0$ atm. Consequently, the first and the second equations are more accurate.
7. $t_{\text{cr}} \approx 147$ °C.
8. $t_{\text{cr}}=30.0$ °C (2.2 °C).
9. $\rho_{\text{cr}}=0.284$ g/cm³ (2.9%), $t_{\text{cr}}=279.3$ °C (0.7 °C) and $p_{\text{cr}}=28.6$ atm (4.7%).
10. $\rho_{\text{cr}}=0.286$ g/cm³ (3.4%).

SECTION 5.4

1. $C_{\text{eq}}^{\text{g}}=-1.044$ kcal/kg·K (7.6%).
2. $\Delta C_{\text{eq}} \approx -33$, -33 and -39 cal/mol·K.
3. $C_{\text{eq}}^{\text{g}}=-0.93$ cal/g·K (17.7%, 10.9%).
4. $\partial \Delta H/\partial T=1.95$ cal/mol·K.
5. $\Delta H=87.5$ cal/g (4.8%).

6. (1) $\Delta H/T = 151.3 - 25.5 \ln T$; (2) 1.9%, 32.5%. The great error for $T = 295$ K is due to its closeness to the critical point ($T_{cr} = 305.6$ K).

7. (1) $\Delta H_{vap}/T = -3.006 \ln T - 0.098548T + 51.766$; (2) 2022 cal/mol (0.4%).

8. (1) $K \approx 0.361 + 0.074n$; (2) $\Delta H = 3727$ cal/g (6.1%); (3) 5233 (1.74%) and 61.86 cal/g (2.1%).

Chapter Six

SECTION 6.1

1. The volume will grow 33.8 times.
2. 19.9 times, which differs from the experimentally found value by 4.1%.
3. $p = 502$ atm (2.8%).
4. $t = 138$ °C.
5. $V = 105$ cm³ (1%).
6. $V = 63.6$ cm³ (7.6%).
7. (1) $V = 107.0$ cm³ (0.94%); (2) $p = 288.9$ (3.7%).
8. Since the isotherm $\tau = 1.45$ has a minimum (see Fig. 31), then it is impossible to determine p according to the data given—two solutions are possible, namely, $p = 500$ atm ($Z = 1.16$) and $p = 240$ atm ($Z = 0.8$). Additional data are needed to obtain an unambiguous solution.
9. $f = 102$ atm.
10. $\Delta H = -22.3$ cal/g (0.9%).
11. $\Delta T \approx -28$ K.
12. $\Delta C_p = 1.3$ cal/mol·K.
13. $\Delta C_p = 9.79$ cal/mol·K. The error (2.2%) is within the limits of the error of an experiment.
14. According to an H - S diagram $\Delta t = -85$ °C (15 °C).
15. $\mu = 0.26$.

SECTION 6.2

1. $t = 75$ °C (10 °C).
2. $p \approx 17$ atm (9.3%).
3. $\frac{1}{2} \left(\frac{\rho^{li}}{\rho_{cr}} + \frac{\rho^g}{\rho_{cr}} \right) \approx 1.8 - 0.8 \frac{T}{T_{cr}}$.
4. $t_{cr} = 503$ °C, $\rho^g = 0.288$ mol/cm³ (1.3%).
5. $\Delta H \approx 91.5$ kcal.
6. $t_{cr} = 374.2$ °C.
7. $\Delta H = 59.1$ cal/g (3.2%, 1%).
8. $p \approx 219$ kgf/cm² (0.2%).
9. $\Delta H \approx 57.9$ cal/g (0.4%).

Chapter Seven

SECTION 7.1

1. $\log x_{\text{AlBr}_3} = -590.2/T_{\text{AlBr}_3}$, $x_{\text{AlBr}_3} = 0.83$. A comparison of the calculated result with the experimentally found values indicates the possibility of considering the solution an ideal one up to $x_{\text{AlBr}_3} \approx 0.80$.

2. $(\Delta H_{\text{fus}})_{o\text{-C}_6\text{H}_4(\text{NO}_2)_2} = 5220$, $(\Delta H_{\text{fus}})_{m\text{-C}_6\text{H}_4(\text{NO}_2)_2} = 4045$ cal/mol. These values differ from those indicated in the initial conditions respectively by 3.8 and 2.6%. Taking into account the inaccuracy of the experimentally found values of ΔH_{fus} and the assumption that ΔH_{fus} does not depend on T , the results of the calculations should be acknowledged as quite satisfactory.

3. $T_{\text{fus}} = 1073$ K, $\Delta H_{\text{fus}} = 7330$ cal/mol (784 K), 7130 cal/mol (767 K); appr. 7230 cal/mol—mean value (0.1%).

4. $\Delta H = -9090$ cal/mol.

5. The solubility should reduce by approximately 7.8 times (28.1%).

6. (1) $t_{\text{eut}} = 4$ °C and 67% of acetophenone;

(2) the crystal will melt;

(3) the system in equilibrium will contain crystalline chloracetophenone and a solution saturated with chloracetophenone in the ratio 1:1.82, i.e. there will be 64.6% (646 g) of a solution containing 32% of acetophenone, and 35.4% (354 g) of crystalline chloracetophenone;

(4) appr. 0.30 kg;

(5) all three mixtures will begin to melt at $t = t_{\text{eut}}$ (4 °C);

(6) the system in equilibrium will contain crystalline chloracetophenone and a saturated solution with 61.5% of acetophenone; the system in equilibrium will contain crystalline acetophenone and a saturated solution with about 78% of acetophenone;

(7) $t = 42$ °C, $t = 4$, $t = 16$ °C;

(8) 235 g, 613 g;

(9) 1424 g;

(10) 84 kg;

(11) $(\Delta H_{\text{fus}})_1 = 3220$ cal/mol, $(\Delta H_{\text{fus}})_2 = 5520$ cal/mol.

8. Although the points in the coordinates $\log x$ versus $1/T$ are located on a straight line, when this line is continued up to $\log x_{\text{C}_6\text{H}_5\text{OH}} = 0$ the equation $\frac{1}{T} = \frac{1}{(T_{\text{fus}})_{\text{C}_6\text{H}_5\text{OH}}}$ is not obtained. In addition, the quantity $-4.576 \tan \alpha$ is several times greater than $(\Delta H_{\text{fus}})_{\text{C}_6\text{H}_5\text{OH}}$. Indeed, $\Delta H = -4.576 \frac{10(-0.1)}{7.0 \times 0.5 \times 10^{-4}} = 13\,050$ cal/mol. Consequently, the solution even in the first approximation cannot be considered an ideal one. The too high results point to a considerable dissociation of the phenol.

9. $x_{p\text{-C}_6\text{H}_4(\text{CH}_3)_2} = 0.254$ (1.6%) instead of 0.243 (2.8%) by Eq. (7.1).

- 10. $\Delta H=2910$ cal/mol (5.4%).
- 11. $M=87.64$ (2.7%).
- 12. The result indicates the dimerization of the SO_3 molecules in the dioxane.
- 13. 3.3%.
- 14. (1) $\Delta t=0.67$ K; (2) No, practically not.
- 15. The slope of a tangent to the crystallization curve of toluene (at the melting point) will be steeper than that of a tangent to the crystallization curve of hexane approximately 1.9 times.

SECTION 7.2

- 1. $\Delta V=-2.52$ cm³.
- 2. $(x_{\text{C}_2\text{H}_4})_{\text{id}}=0.038$, $(x_{\text{C}_2\text{H}_4})_{\text{ex}}=0.022$. Since the discrepancy between the calculated and the experimentally found values of $x_{\text{C}_2\text{H}_4}$ is beyond the limits of the errors of experiment (due to the insufficient purity of the alcohol, the inaccurate value of the density of the alcohol, etc.), a solution of acetylene in alcohol at the indicated temperature and concentration cannot be considered as an ideal one.
- 3. The mean discrepancy between the calculated and experimentally found values is about 3%, and for this reason the solution may be considered as an ideal one.
- 5. 5.26 g.
- 6. $(x_{\text{N}_2})_{\text{id}}=17.6 \times 10^{-4}$, 0.260 (2.4%).
- 7. 20.7 cm³ (0.5%), 9.34 g.
- 8.

Gas	Gas liberated		Gas remaining in solution	
	m ³ in standard conditions	%	m ³ in standard conditions	%
CO ₂	22.92	94.1	4.65	98.5
H ₂ S	0.13	0.5	0.07	1.5
H ₂	0.92	3.8	< 0.005	—
N ₂	0.28	1.2	< 0.005	—
CO	0.10	0.4	< 0.005	—
Total	24.35	100.0	4.72	100.0

- 9. $V=0.2$ m³.
- 10. $k=1620$.
- 11. $x_{\text{H}_2}=0.0678$ (4.5%).

SECTION 7.3

1. (1) 10% of phenol, 35% of water; (2) the first is greater than the second; (4) $t=57.5\text{ }^{\circ}\text{C}$; (5) in the first one; (7) 10.5 and 65.0% H_2O ; 8.26 and 17.4 g; (8) 28 g of water; (9) about 500 g of water; (10) about 15.5 g of phenol.
2. 58% of water (0.0%).
3. 15% of aniline (6.2%).
4. (1) $(w_1+w_2)/2=52.87+0.0263t$, where w_1 and w_2 are the weight per cents of benzene; (2) at $t=75\text{ }^{\circ}\text{C}$ the system will be homogeneous.
5. (1) $[\text{C}_6\text{H}_6]:[\text{H}_2\text{O}]=6.33:1.515$ g of $\text{C}_2\text{H}_5\text{OH}$; (2) a solution containing 10% of C_6H_6 , 50.5% of $\text{C}_2\text{H}_5\text{OH}$ and 39.9% of H_2O will be in equilibrium with a solution containing 3.5% of H_2O , 10.5% of $\text{C}_2\text{H}_5\text{OH}$ and 86% of C_6H_6 in the ratio of 2.8:1; (3) about 120 g of $\text{C}_6\text{H}_6+1080$ g of H_2O , 90% of C_6H_6 , 7% of $\text{C}_2\text{H}_5\text{OH}$, 3% of H_2O ; (4) from pure benzene to a solution containing 91.5% of C_6H_6 , 2.5% of H_2O and 6% of $\text{C}_2\text{H}_5\text{OH}$ and from a solution containing 32% of C_6H_6 , 47.5% of $\text{C}_2\text{H}_5\text{OH}$ and 20.5% of H_2O in the direction of a further decrease in the benzene concentration.
6. 50.4% of $\text{C}_2\text{H}_5\text{OH}$ (6.4%). With a view to the difficulty (and hence the inaccuracy) of determining the composition of the mixtures, and also to the fact that a value obtained only for one pair of the conjugated solutions has been taken for the quantity k in Eq. (7.9), the result should be considered as satisfactory.
8. (1) Yes, it may, since the computed concentration in a saturated solution differs from the experimentally found value by 2.0%; (2) 0.5384.
9. 28.58 dm³, 95.3%.
10. 89.8%, 99.37%.

Chapter Eight

SECTION 8.1

1. $p=290.5\text{ mm Hg}$ (0.96%) for $x_{\text{methylal}}=0.1882$ and $p=309.9\text{ mm Hg}$ (0.84%) for $x_{\text{methylal}}=0.3588$.
2. (1)

x_{methylal}	p_{methylal} , mm Hg	p_{acetone} , mm Hg	p , mm Hg
0.1	74.8	312.9	387.7
0.2	142.1	280.7	422.8
0.3	203.2	249.3	452.6
0.4	261.6	218.1	479.7
0.5	316.8	186.5	503.3
0.6	370.6	153.9	524.5
0.7	421.4	119.6	543.7
0.8	478.2	83.1	561.3
0.9	533.7	43.4	577.1

(3) for these two compositions the discrepancy is less than 0.5%.

3. $p_{\text{C}_2\text{H}_5\text{Cl}}=770$ mm Hg and $p_{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5}=291$ mm Hg, which differ from the indicated values by 0.3 and 4%, respectively. These results are within the limits of the error of experimental data.

6. $p=127.5$ mm Hg.

7. 17.08 mole% of ortho-, 27.23 mole% of meta- and 55.69 mole% of para-xylene.

8. $p \leq 168.8$ mm Hg, $x_{\text{C}_2\text{H}_6}^g=0.505$.

SECTION 8.2

1. $p=220$ mm Hg.

2. (1) $p=220$ mm Hg; (2) $p=145$ mm Hg.

4. (1) $t=76^\circ\text{C}$; (2) by 15.5 K.

5. 65.8%.

6. (1) 83.4 kg; (2) approximately 10 times.

7. 125 kg; the increase in the consumption of steam is due to the fact that as a result of lowering of the temperature the vapour of the liquid being distilled will condense first of all.

Chapter Nine

SECTION 9.1

1. $\Delta H^\circ = -7700$ cal/mol (4.6%).

2. $\Delta H^\circ = -103\,410$ cal/mol.

3. (1) $\log K_1 \approx 1640T^{-1} - 0.43$; (2) $t \approx 1217^\circ\text{C}$.

4. $\Delta H^\circ \approx 4010$ cal/mol.

5. $\Delta H^\circ = 32\,600$ cal/mol (23.2%). The considerable discrepancy is due to the circumstance that the pressures of dissociation in the given investigation were lowered (obviously owing to insufficient purity of the calcium carbonate).

6. 2.28 kg.

7. $\log K_p = 1.685$. The considerable discrepancy is due to the fact that the calculations were based on the heat of the reaction at $T=298$ K.

8. $K_p = 1.10$ (35%).

9. $\log K_p = -8.273$ (8%).

10. $\Delta G_{1000}^\circ = 25\,700$ cal/mol (9%).

11. $K_p = 11.6 \times 10^{-6}$.

12. $\log K_p = -3853T^{-1} + 3.562 \log T - 1.508 \times 10^{-3}T - 0.1207 \times 10^{-6}T^2 - 4.216$; $\log K_p = -3.09$; the discrepancy is about 0.3 or $4.576 \times 500 \times 0.3 = 686$ cal.

13. $\Delta H^\circ = -43\,880 - 19.71T + 0.010\,45T^2$; $\Delta H_{298}^\circ = -48\,830$ cal/mol. According to tabulated data $\Delta H_{298}^\circ = -49\,250$ cal/mol, which differs from the found value by 0.9%.

14. $K_p = 54.3$.

15. $\log K_p = -9070T^{-1} - 11.57 \log T + 3.192 \times 10^{-3}T - 0.05723 \times 10^{-5}T^2 + 13.8$ and $\Delta G^\circ = 41\,500 + 22.983T \ln T - 14.6064 \times 10^{-3}T^2 + 0.2618 \times 10^{-6}T^3 - 63T$; $\Delta H_{298}^\circ \approx -47\,000$ cal/mol (4.6%).
16. $T\Delta S = 18\,100$ cal/mol.
17. $(\Delta H_{298}^\circ)_{\text{III}} = -7590$ cal/mol, $(\Delta H_{298}^\circ)_{\text{IV}} = -18\,515$ cal/mol.
18. (1) A rise of the temperature shifts equilibrium to the left; (2) $\Delta H^\circ = -1970$ cal/mol (410 cal).
19. $\log K_p = 3953T^{-1} - 8.550 \log T + 1.7918 \times 10^{-3}T - 0.0014 \times 10^{-6}T^2 + 15.384$; $\Delta G^\circ = 20\,690$ cal/mol.
20. $\Delta G_{700}^\circ = 126\,570$ cal/mol, $\Delta G_{1000}^\circ = 110\,610$ cal/mol.

SECTION 9.2

1. $T = 369.6$ K (1.0 K).
2. $\Delta G_{298}^\circ = -15\,721$ cal/mol.
3. $\log K_p = -2.00$.
4.

T , K	300	600	900	1200	1500
$\log K_p$	45.15	20.48	12.24	8.02	5.67
Discrepancy	0.10	0.42	0.40	0.28	0.38
5. $T \approx 710$ K (105 K) and ≈ 690 K (73 K).
6. $\log K_p = 7155T^{-1} - 1.75 \log T - 1.8$; $(\log K_p)_{773} = 2.40$.
7. $S^\circ = 54.8$ cal/mol·K.
8. $S^\circ = 49.14$ cal/mol·K.
9. $K_p = 2.08 \times 10^{-2}$ (19.5%).
10. $\Delta G_{298}^\circ = 8705$ cal/mol, $K_{298} = 4.161 \times 10^{-7}$.
11. (1) $\Delta G^\circ = 14\,400$ cal/mol (2.1%); (2) $\Delta G_{298}^\circ = -39\,150$ cal/mol (0.2%), $\Delta H_{298}^\circ = -48\,790$ cal/mol (0.6%) and $S_{298}^\circ = 56.01$ cal/mol·K (1.71 cal).
12. $\log K_p = 2450T^{-1} - 6.824$.
13. $K_p = 2.05 \times 10^{-2}$.
14.

T	log K _p				
	Problem	Example 7			Exact data
		(a)	(b)	(c)	
400	−13.340	−13.371	−13.339	−13.340	−13.285
800	−1.946	−2.108	−1.825	−1.999	−1.963
1200	1.811	1.646	2.151	1.733	1.757

15. (1) $\Delta G_{298}^\circ = -25\,120$ cal/mol (0.44%); (2) $S_{298}^\circ = 16.3$ cal/mol·K (0.7%).
16. $\Delta H_{298}^\circ = -25\,160$ cal/mol (1.04%).
17. $K_p = 3.787$.

Chapter Ten

SECTION 10.1

2. $K=311.9$.
3. 21.2% by weight of alcohol.
4. (1) $(K_p)_{2400}=0.00142$, $(K_p)_{3000}=0.00855$; (2) $\Delta H \approx 21\,400$ cal/mol (0.9%). In the given case $\Delta C_p \approx 0$.
5. $K_{III}=0.31$ (0.06).
6. 94.4% of SO_3 .
7. (1) 7.12% of SO_3 , 0.13% of SO_2 , 7.83% of O_2 and 84.92% of N_2 . The degree of transition equals 0.98; (2) 6.49% of SO_3 , 0.93% of SO_2 , 8.09% of O_2 and 84.49% of N_2 .
8. 37% of NH_3 .
9. $K_f=1.6 \times 10^{-3}$; $K_v=0.101$.
10. $q=6.6 \times 10^{-4}$.
11. (1) $\Delta H^\circ \approx 17\,000$ cal/mol of $(\text{CH}_3\text{COOH})_2$; (2) 1:2.3.

SECTION 10.2

1. $p=3.96$ atm.

2.

p , atm	100	300	500	700	900
NH_3 in mixture, %	13.4	30.7	41.9	49.9	56.0

From a comparison of the results of solving the present problem and Example 2 it follows that the presence of inert gases in an amount of 40% leads to the same effect as a decrease in the pressure from $p=300$ atm to approximately 100 atm with an unchanging composition of the gas.

4. (1) 13.0% of NH_3 ; (2) the content of the inert gas grows by 0.26%; (3) the ratio will change adversely—instead of the original value of 2.86 it will be 2.81. (If in the initial mixture $[\text{H}_2]:[\text{N}_2]$ had exceeded 3, this ratio in the course of the reaction would have increased.)

5. 0.836 mole of H_2 .

6. The temperature should be reduced by 4 K.

7. About 3.5 volumes of steam must be taken per volume of the steam and gas mixture.

8. $x \approx 0.091$ (9.1% of CH_3OH).

9. $p \geq 1.59$ atm.

10. (1) about: up to 750 K (I); 750 K (II); 670 K (III); (2) the temperature will rise; (3) in this case the equation will have the form

$$x = \frac{(m+n)(pK_p+1) - \sqrt{(m+n)^2(pK_p+1)^2 - 4(pK_p+1)n \cdot mpK_p}}{2(pK_p+1)}$$

11. The conditions are even more unfavourable than in Example 7. The result could have been predicted beforehand, since the reaction proceeds with an increase in the volume, and for this reason the dilution of the mixture with an inert gas has a negative action.

12. $t \leq 245.5^\circ\text{C}$.

13. The reaction proceeds from the left to the right; $\Delta G^\circ = -2443\text{ cal/mol}$.

14. $\Delta G^\circ = 14\,255\text{ cal/mol}$, which points to the impossibility of the reaction at low temperatures. Experimental data confirm this conclusion.

SECTION 10.3

1. In the temperature interval considered the reactions (I), (II) and (IV) should proceed practically to the end; for this reason it may be assumed that there will be no oxygen in an equilibrium mixture and its composition will be determined only by the equilibrium of the reaction (III).

2.

T, K	Composition of equilibrium mixture, mol %								
	n-	2-	3-m	3-e	2,2-	2,3-	2,4-	3,3-	2,2,3-
400	3.2	11.9	12.5	1.3	15.3	30.9	7.9	10.2	6.8
600	9.3	16.4	21.8	2.7	6.8	26.6	5.5	7.4	3.5
800	14.1	17.5	26.0	3.5	4.4	21.8	4.2	6.1	2.4

It follows from the results of the calculations that with a growth in the temperature, the stability of alkanes having a normal structure with respect to that of their isomers increases.

4. (2)

T	log K_p	
	I	(II-IV)
600	2.82	2.87
700	1.32	1.50
800	0.163	0.33

5. See the following table.

<i>t</i>	Compo- sition of gas, %	In the presence of carbon				In the absence of carbon			
		[CO ₂]:[CH ₄]=1:1		[CO ₂]:[CH ₄]=5:1		[CO ₂]:[CH ₄]=1:1		[CO ₂]:[CH ₄]=5:1	
		<i>p</i> =1	<i>p</i> =20	<i>p</i> =1	<i>p</i> =20	<i>p</i> =1	<i>p</i> =20	<i>p</i> =1	<i>p</i> =20
700	CO ₂	10.21	18.86	26.70	55.84	4.18	21.21	38.30	47.60
	CO	30.00	9.25	51.15	15.90	44.65	29.60	36.80	27.80
	H ₂	47.69	26.69	16.50	8.40	41.75	14.57	14.33	9.90
	CH ₄	1.70	10.20	0.19	1.01	6.80	27.95	0.06	3.80
	H ₂ O	10.40	35.00	5.46	18.85	2.62	6.67	10.51	10.90
900	CO ₂	0.63	7.05	1.68	19.91	0.31	4.69	36.00	37.76
	CO	48.73	36.30	81.24	59.65	48.10	46.90	38.90	38.70
	H ₂	49.45	40.83	16.63	13.71	50.40	31.32	11.15	10.17
	CH ₄	0.35	5.10	0.04	0.57	0.75	9.42	0.00	0.07
	H ₂ O	0.84	10.72	0.41	6.16	0.44	4.67	13.95	13.30

APPENDICES

1. ATOMIC MASSES OF SELECTED ELEMENTS (1973)

Element	Symbol	Atomic number	Atomic weight
Aluminium	Al	13	26.981 54
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Barium	Ba	56	137.34
Beryllium	Be	4	9.012 18
Bismuth	Bi	83	208.9804
Boron	B	5	10.81
Bromium	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Carbon	C	6	12.011 15
Cerium	Ce	58	140.12
Cesium	Cs	55	132.9054
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Fluorine	F	9	18.9984
Gallium	Ga	31	69.72
Gold	Au	79	196.9665
Helium	He	2	4.002 60
Hydrogen	H	1	1.007 97
Indium	In	49	114.82
Iodine	I	53	126.9044
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.9380
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Nitrogen	N	7	14.0067
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.973 76
Platinum	Pt	78	195.09
Potassium	K	19	39.102
Radium	Ra	88	226.0254
Radon	Rn	86	222

(concluded)

Element	Symbol	Atomic number	Atomic weight
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulphur	S	16	32.064
Tantalum	Ta	73	180.9479
Tellurium	Te	52	127.60
Thallium	Tl	81	204.37
Thorium	Th	90	232.0381
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

2. CORRECTIONS FOR THE APPROXIMATE CALCULATION
OF THE STANDARD HEATS OF FORMATION, HEAT CAPACITIES
AND ENTROPIES
FOR THE IDEALIZED GASEOUS STATE

A. Properties of Basic Substances

Substance	ΔH_{298}° , kcal/mol	Coefficients of equation $C_p=f(T)$			ΔS_{298}° , entropy units
		a	$b \times 10^3$	$c \times 10^6$	
Methane	—17.89	3.79	16.62	—3.24	44.50
Cyclopentane	—18.46	—9.02	109.28	—40.23	70.00
Cyclohexane	—29.43	—11.53	139.65	—52.02	71.28
Benzene	19.82	—4.20	91.30	—36.63	64.34
Naphthalene	35.40	3.15	109.40	—34.79	80.70
Methylamine	—7.10	4.02	30.72	—8.70	57.70
Dimethylamine	—7.80	3.92	48.31	—14.09	65.20
Trimethylamine	—10.90	3.93	65.85	—19.48	—
Diethyl ether	—46.00	6.42	39.64	—11.45	63.70
Formamide	—49.50	6.51	25.18	—7.47	—

**B. Corrections for Substitution
of the Primary Hydrogen Atom by CH₃ Groups**

Basic group	$\Delta(\Delta H_{298}^{\circ})$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS_{298}° , entr. units
Methane	—2.50	—2.00	23.20	—9.12	10.35
Cyclopentane					
first substitution	—7.04	1.87	17.55	—6.68	11.24
second substitution:					
1,1	—7.55	—0.67	24.29	—10.21	4.63
1,2 (<i>cis</i>)	—5.46	—0.01	22.69	—9.46	6.27
1,2 (<i>trans</i>)	—7.17	0.28	21.97	—9.18	6.43
1,3 (<i>cis</i>)	—6.43	0.28	21.97	—9.18	6.43
1,3 (<i>trans</i>)	—6.97	0.28	21.97	—9.18	6.43
additional correction for each following sub- stitution	7.00	—	—	—	—
Cyclohexane					
correction for increase of ring for each added carbon atom	—10.97	—2.51	30.37	—11.79	1.28
first substitution in ring	—7.56	2.13	18.66	—5.71	10.78
second substitution in ring:					
1,1	—6.27	—2.14	25.69	—10.09	5.18
1,2 (<i>cis</i>)	—4.16	—0.65	22.19	—8.84	7.45
1,2 (<i>trans</i>)	—6.03	—0.06	22.59	—2.56	6.59
1,3 (<i>cis</i>)	—7.18	—0.34	21.49	—7.95	6.48
1,3 (<i>trans</i>)	—5.21	0.29	19.29	—7.23	7.86
1,4 (<i>cis</i>)	—5.23	0.29	19.29	—7.23	6.48
1,4 (<i>trans</i>)	—7.13	—0.72	23.79	—9.91	5.13
additional correction for each following substi- tution	—7.00	—	—	—	—
Benzene					
first substitution	—7.87	0.78	16.68	—5.41	12.08
second substitution:					
1,2	—7.41	4.27	9.72	—1.87	7.89
1,3	—7.83	0.77	17.46	—6.19	9.07
1,4	—7.66	1.76	13.45	—3.41	7.81
third substitution:					
1,2,3	—6.83	1.41	12.78	—2.71	9.19
1,2,4	—7.87	1.61	12.72	—2.77	10.42
1,3,5	—7.96	2.41	11.30	—1.90	6.66
Naphthalene					
first substitution	—4.50	0.36	17.65	—5.88	12.00
second substitution:					
1,2	—6.30	5.20	6.02	—1.18	8.10
1,3	—6.50	1.72	14.18	—3.76	9.20
1,4	—8.00	1.28	14.57	—3.98	7.80
Methylamine	—5.70	—0.10	17.52	—5.35	—
Dimethylamine	—6.30	—0.10	17.52	—5.35	—
Trimethylamine	—4.10	—0.10	17.52	—5.35	—
Formamide substitution to C atom	—9.00	6.11	—1.75	4.75	—

C. Corrections for Substitution of the Secondary Hydrogen Atom by CH₃ Groups

A	B	$\Delta(\Delta H_{298}^\circ)$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS_{298}° , entr. units
1	1	-4.75	0.49	22.04	-8.96	10.10
1	2	-4.92	1.09	17.79	-6.47	9.18
1	3	-4.42	1.00	19.88	-8.03	9.72
1	4	-5.0	1.39	17.12	-5.88	11.00
1	5	-4.68	1.09	18.71	-7.16	10.76
2	1	-6.31	-0.30	21.74	-8.77	5.57
2	2	-6.33	-0.64	23.38	-9.97	7.15
2	3	-5.25	0.80	19.27	-7.70	6.53
2	4	-3.83	2.52	16.11	-5.88	7.46
2	5	-6.18	0.37	19.25	-7.72	6.72
3	1	-8.22	-0.28	24.21	-10.49	2.81
3	2	-7.00	-0.93	24.73	-8.95	3.87
3	3	-5.19	-3.27	30.96	-14.06	3.99
3	4	-4.94	-0.14	27.57	-10.27	1.88
3	5	-9.20	0.42	16.20	-4.68	1.30
In esters or ethers (1—0—)		-7.00	-0.01	17.58	-5.33	14.00
Substitution of H in acid by —CH ₃ group with formation of ester		9.50	0.44	16.63	-4.95	16.70

D. Corrections for Substitution of Single Bonds by Multiple Ones

Kind of bond	$\Delta(\Delta H_{298}^\circ)$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS_{298}° , entr. units
1=1	32.88	0.21	-8.28	1.36	-2.40
1=2	30.00	1.12	-11.40	3.32	-0.21
1=3	28.23	2.18	-15.62	6.42	-0.11
2=2 (<i>cis</i>)	28.39	-3.57	0.14	1.08	-1.19
2=2 (<i>trans</i>)	27.40	1.27	-12.77	3.88	-2.16
2=3	26.72	-2.02	-10.42	3.83	-0.28
3=3	25.70	-0.41	-15.14	6.39	-0.66
1≡1	74.58	4.72	-24.36	6.29	-9.85
2≡2	65.50	1.00	-25.70	-9.50	-3.97
1≡2	69.52	-3.16	-26.37	8.82	-4.19

E. Additional Corrections for Final Structure of Hydrocarbons

	$\Delta(\Delta H_{298}^\circ)$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS_{298}° , entr. units
Additional correction for each long side chain in ring:					
more than 2C in side chain of cyclopentane	-0.45	-0.48	1.50	1.15	0.12
more than 2C in side chain of cyclohexane	0.32	0.76	2.10	1.30	-0.39
more than 4C in side chain of benzene	-0.70	0.22	-0.20	0.08	-0.62
Additional correction for dou- ble bond introduced:					
for conjugated double bonds	13.16	2.24	1.16	-0.25	-3.74
for alternating double bonds	-4.28	-0.94	3.88	-3.49	-5.12
for double bond adjacent to aromatic ring:					
in side chain less than 5C long	-2.00	1.01	-3.24	1.31	-2.65
in side chain over 4C long	-1.16	1.01	-3.24	1.31	-2.65

F. Corrections for Groups Substituting CH_3

Group	$\Delta(\Delta H_{298}^\circ)$, kcal/mol	Δa	$\Delta b \times 10^3$	$\Delta c \times 10^6$	ΔS_{298}° , entr. units
-OH (aliphatic, meta, para)	-32.70	3.17	-14.86	5.59	2.60
-OH (ortho)	-47.70	—	—	—	—
-NO ₂	1.20	6.30	-19.53	10.63	2.00
-CN	39.00	3.64	-13.92	4.53	4.00
-Cl; for the first Cl at a carbon atom	0	2.19	-18.85	6.26	0
-Cl; for each following one	4.50	—	—	—	—
-Br	10.00	2.81	-19.41	6.33	3.00*
-F	-35.00	2.24	-23.61	11.79	-1.00*
-I	24.80	2.73	-17.37	4.09	5.00*
=O (aldehyde)	-12.90	3.61	-55.72	22.72	-12.30
-COOH	-87.00	8.50	-15.07	7.94	15.40
=O (ketone)	-13.20	5.02	-66.08	30.21	-2.40
-SH	15.80	4.07	-24.96	12.37	5.20
-C ₆ H ₅	32.30	-0.79	53.63	-19.21	21.70
-NH ₂	12.30	1.26	-7.32	2.23	-2.80

* The corrections for the entropy of halogens calculated for methyl derivatives should be increased by unity. For example, the entropy of methyl chloride is 44.4 (basic group) + 10.4 (substitution of a primary hydrogen atom by a $-\text{CH}_3$ group) + 0 (substitution by chlorine) + 1.

3. THERMODYNAMIC QUANTITIES FOR A ONE-DIMENSIONAL HARMONIC OSCILLATOR

$\frac{\Theta}{T}$	C	$\frac{U - U_0}{T} = \frac{1}{T} \int_0^T C dT$	S	$\frac{G - U_0}{T} = \int_0^T \frac{dT}{T^2} \int_0^T C dT$	$\frac{\Theta}{T}$	C	$\frac{U - U_0}{T} = \frac{1}{T} \int_0^T C dT$	S	$\frac{G - U_0}{T} = \int_0^T \frac{dT}{T^2} \int_0^T C dT$
0	1.986	1.986	∞	∞	2.30	1.302	0.510	0.719	0.210
0.10	1.983	1.888	6.560	4.67	2.40	1.256	0.476	0.665	0.189
0.15	1.981	1.841	5.730	3.89	2.50	1.210	0.444	0.614	0.170
0.20	1.979	1.761	5.190	3.39	2.60	1.164	0.414	0.568	0.153
0.25	1.976	1.747	4.740	2.99	2.70	1.119	0.386	0.525	0.138
0.30	1.974	1.702	4.390	2.68	2.80	1.074	0.360	0.485	0.125
0.35	1.967	1.659	4.080	2.42	2.90	1.030	0.336	0.448	0.112
0.40	1.960	1.615	3.820	2.20	3.00	0.986	0.312	0.414	0.102
0.45	1.952	1.572	3.600	2.02	3.10	0.943	0.291	0.382	0.092
0.50	1.945	1.531	3.380	1.85	3.20	0.901	0.270	0.353	0.083
0.55	1.938	1.490	3.200	1.709	3.30	0.860	0.251	0.326	0.075
0.60	1.928	1.449	3.031	1.581	3.40	0.820	0.233	0.301	0.067
0.65	1.918	1.410	2.877	1.467	3.50	0.781	0.217	0.277	0.061
0.70	1.908	1.371	2.736	1.364	3.60	0.744	0.201	0.256	0.055
0.75	1.896	1.334	2.604	1.270	3.70	0.707	0.187	0.236	0.050
0.80	1.884	1.297	2.482	1.185	3.80	0.672	0.173	0.218	0.045
0.85	1.871	1.260	2.369	1.108	3.90	0.637	0.160	0.201	0.041
0.90	1.858	1.224	2.262	1.037	4.00	0.604	0.148	0.185	0.037
0.95	1.844	1.191	2.162	0.972	4.20	0.542	0.127	0.157	0.030
1.00	1.829	1.156	2.068	0.911	4.40	0.484	0.109	0.133	0.025
1.05	1.814	1.123	1.979	0.856	4.60	0.431	0.0927	0.113	0.020
1.10	1.798	1.090	1.895	0.804	4.80	0.383	0.0790	0.096	0.016
1.15	1.782	1.058	1.815	0.756	5.00	0.339	0.0673	0.081	0.014
1.20	1.765	1.027	1.740	0.712	5.20	0.300	0.0573	0.068	0.011
1.25	1.747	0.997	1.668	0.671	5.40	0.262	0.0487	0.058	0.009
1.30	1.729	0.968	1.600	0.632	5.60	0.232	0.0413	0.049	0.007
1.35	1.711	0.939	1.535	0.596	5.80	0.204	0.0353	0.041	0.006
1.40	1.692	0.911	1.437	0.563	6.00	0.178	0.0297	0.035	0.005
1.45	1.673	0.883	1.414	0.531	6.40	0.136	0.0251	0.024	0.003
1.50	1.659	0.856	1.358	0.502	6.80	0.103	0.0151	0.017	0.002
1.55	1.633	0.829	1.304	0.474	7.20	0.077	0.0107	0.014	0.001
1.60	1.612	0.804	1.252	0.448	7.60	0.057	0.0076	0.009	0.001
1.65	1.592	0.779	1.203	0.424	8.00	0.0427	0.0053	0.006	0.001
1.70	1.570	0.755	1.156	0.401	8.40	0.032	0.0038	0.004	0.000
1.75	1.549	0.731	1.111	0.379	8.80	0.023	0.0030	0.003	
1.80	1.527	0.708	1.067	0.359	9.20	0.017	0.0018	0.002	
1.85	1.505	0.686	1.026	0.340	9.60	0.012	0.0013	0.001	
1.90	1.483	0.664	0.986	0.322	10.00	0.009	0.0009	0.001	
1.95	1.461	0.633	0.948	0.305	11	0.004	0.004		
2.00	1.439	0.622	0.911	0.289	12	0.0017	0.0001		
2.10	1.393	0.582	0.842	0.259	13	0.0007			
2.20	1.348	0.545	0.778	0.233					

4. CHARACTERISTIC FREQUENCIES
FOR CALCULATING THE HEAT CAPACITIES OF GASES BY EQ. (2.16)

Bond	ν_i	δ_i	Bond	ν_i	δ_i
C—C (aliphatic)	989	390	S—S	500	260
C=C (aliphatic, symmetrical)	1618	599	S—H	2570	1050
C=C (aliphatic, asymmetrical)	1664	421	C—N	990	390
C≡C (aliphatic)	2215	333	C=N	1620	845
C=C (aliphatic)	1618	844	N—H	2920	1320
C—H (aliphatic)	2914	1247	N—O	1030	205
C—H (aromatic)	3045	1318	C=S	1050	530
C—F	1050	530	N—N	990	390
C—Cl	650	330	O—H	3420	1150
C—Br	560	280	C=O	1700	390
C—I	500	260	C—O	1030	205
C—S	650	330	N=O	1700	390

5. TABLE OF TARASOV (C_1 , C_2)
AND DEBYE (C_3) FUNCTIONS

$\frac{\theta}{T}$	$\frac{T}{\theta}$	C_1	C_2	C_3	$\frac{\theta}{T}$	$\frac{T}{\theta}$	C_1	C_2	C_3
0.0	∞	5.957	5.957	5.957	4.8	0.208	—	2.81	2.34
0.2	5.000	5.937	—	5.94	5.0	0.200	3.62	2.68	2.197
0.4	2.500	5.92	—	5.91	5.2	0.192	—	2.54	2.06
0.6	1.667	5.89	—	5.85	5.4	0.185	—	2.41	1.93
0.8	1.250	5.85	—	5.77	5.6	0.179	—	2.31	1.81
1.0	1.000	5.79	5.76	5.67	5.8	0.172	—	2.20	1.69
1.2	0.883	5.73	5.64	5.55	6.0	0.167	3.14	2.09	1.582
1.4	0.714	5.65	5.51	5.41	6.2	0.161	—	1.98	1.48
1.6	0.625	5.55	5.39	5.26	6.4	0.156	—	1.88	1.39
1.8	0.556	5.46	5.25	5.09	6.6	0.151	—	1.79	1.30
2.0	0.500	5.36	5.08	4.918	6.8	0.147	—	1.71	1.21
2.2	0.455	—	4.94	4.74	7.0	0.143	2.75	1.63	1.137
2.4	0.417	—	4.78	4.54	8.0	0.125	2.42	1.34	0.823
2.6	0.385	—	4.61	4.35	9.0	0.111	2.17	1.056	0.604
2.8	0.357	—	4.42	4.15	10.0	0.100	1.949	0.86	0.452
3.0	0.333	4.81	4.24	3.95	11.0	—	—	—	0.343
3.2	0.313	—	4.07	3.75	12.0	0.083	1.630	0.592	0.267
3.4	0.294	—	3.90	3.56	13.0	—	—	—	0.210
3.6	0.278	—	3.74	3.36	14.0	0.071	1.357	0.432	0.169
3.8	0.263	—	3.57	3.18	15.0	—	—	—	0.137
4.0	0.250	4.17	3.41	2.996	16.0	0.063	1.226	0.341	0.113
4.2	0.238	—	3.25	2.82	18.0	—	—	—	0.079
4.4	0.227	—	3.09	2.65	20.0	0.050	0.978	0.215	0.058
4.6	0.217	—	2.94	2.50					

6. MEAN HEAT CAPACITIES OF SELECTED GASES BETWEEN 0 AND t °C

<div>Gas</div> <div>t</div>	H ₂	N ₂	O ₂	CO	NO	H ₂ O	CO ₂	N ₂ O	SO ₂	Air	CH ₄	C ₂ H ₄	C ₂ H ₂
100	6.92	6.97	7.05	6.97	7.14	8.03	9.17	9.79	9.74	6.96	8.73	11.45	11.12
200	6.95	7.00	7.15	7.00	7.17	8.12	9.65	10.12	10.15	7.01	9.48	12.64	11.79
300	6.97	7.04	7.26	7.06	7.22	8.22	10.06	10.45	10.52	7.06	10.20	13.73	12.36
400	6.98	7.09	7.38	7.12	7.30	8.34	10.40	10.74	10.84	7.13	10.88	14.76	12.81
500	6.99	7.15	7.49	7.19	7.38	8.47	10.75	11.02	11.11	7.20	11.53	15.69	13.21
600	7.01	7.21	7.59	7.27	7.46	8.60	11.03	11.24	11.35	7.27	12.15	16.52	13.58
700	7.03	7.27	7.68	7.34	7.54	8.74	11.28	11.50	11.55	7.34	12.74	17.26	13.90
800	7.06	7.35	7.77	7.43	7.62	8.89	11.50	11.71	11.72	7.42	13.28	18.07	14.22
900	7.09	7.42	7.85	7.50	7.70	9.04	11.70	11.90	11.88	7.49	13.79	18.62	14.49
1000	7.12	7.49	7.92	7.57	7.76	9.18	11.88	12.07	12.01	7.56	14.27	19.24	14.75
1100	7.15	7.56	7.98	7.64	7.83	9.32	12.05	12.21	12.13	7.62			
1200	7.20	7.62	8.04	7.70	7.89	9.45	12.19	12.35	12.23	7.68			
1300	7.24	7.67	8.11	7.76	7.94	9.58	12.32	12.48	12.33	7.73			
1400	7.28	7.73	8.16	7.81	7.99	9.72	12.45	12.60	12.41	7.78			
1500	7.32	7.78	8.20	7.85	8.03	9.84	12.56	12.69	12.48	7.84			
1600	7.36	7.82	8.24	7.90	8.08	9.96	12.66	12.78	12.55	7.88			
1700	7.40	7.86	8.28	7.94	8.12	10.09	12.75	12.88	12.61	7.92			
1800	7.45	7.91	8.33	7.98	8.15	10.20	12.84	12.95	12.67	7.96			
1900	7.49	7.94	8.38	8.02	8.19	10.30	12.92	13.01	12.71	7.99			
2000	7.53	7.98	8.42	8.05	8.22	10.41	12.99	13.09	12.77	8.03			
2100	7.57	8.01	8.45	8.09	8.26	10.52	13.06	13.17	12.81	8.06			
2200	7.62	8.05	8.48	8.12	8.29	10.61	13.13	13.21	12.85	8.08			
2300	7.66	8.08	8.52	8.15	8.31	10.71	13.19	13.28	12.89	8.12			
2400	7.70	8.10	8.56	8.18	8.34	10.79	13.24	13.33	12.93	8.14			
2500	7.74	8.14	8.59	8.21	8.36	10.87	13.30	13.38	12.96	8.18			
2600	7.78	8.17	8.63	8.24	8.38	10.96	13.34	13.42	12.99	8.20			
2700	7.81	8.19	8.65	8.46	8.40	11.03	13.39	13.46	13.02	8.23			
2800	7.85	8.22	8.68	8.28	8.42	11.11	13.43	13.51	13.04	8.25			
2900	7.89	8.24	8.72	8.30	8.44	11.18	13.48	13.55	13.07	8.27			
3000	7.92	8.26	8.76	8.32	8.45	11.23	13.52	13.59	13.10	8.29			

7. CONSTANTS OF VAN-DER-WAALS EQUATION
FOR SELECTED GASES

Substance	$a \times 10^{-6}$	b	Substance	$a \times 10^{-6}$	b
H ₂	0.245	26.6	CO ₂	3.604	42.8
He	0.0334	23.2	CH ₄	2.264	42.78
NH ₃	4.192	37.3	C ₂ H ₂	4.398	51.37
N ₂	1.348	38.6	C ₂ H ₄	4.48	57.19
O ₂	1.362	31.8	C ₃ H ₈	9.249	90.23

8. CRITICAL TEMPERATURES
AND PRESSURES OF SELECTED LIQUIDS

Substance	t_{cr}	p_{cr}	Substance	t_{cr}	p_{cr}
Ar	−122.2	48.0	C ₂ H ₂ , acetylene	36	62
Br ₂	302.2	121	C ₂ H ₄ , ethylene	9.7	50.8
Cl ₂	144.0	76.1	CH ₃ COOH, acetic acid	321.6	57.2
H ₂	−240.0	12.8	C ₂ H ₆ , ethane	32.3	48.2
H ₂ O	374.15	218.5	C ₂ H ₅ OH, ethanol	243.0	63.1
He	−268.0	2.26	CH ₃ OCH ₃ , methyl ether	126.9	53
N ₂	−147.1	33.5	CH ₃ COCH ₃ , acetone	235.0	47.0
NH ₃	132.4	111.5	CH ₃ COOCH ₃ , methyl ace- tate	233.7	46.0
Ne	−228.8	26.9	C ₃ H ₈ , propane	96.8	42.0
O ₂	−118.8	49.7	C ₃ H ₈ O, propanol	263.0	53.0
SO ₂	157.3	77.8	C ₂ H ₅ OCOCH ₃ , ethyl ace- tate	250.1	37.8
SO ₃	218.2	83.8	C ₄ H ₁₀ , <i>n</i> -butane	152.5	36.0
CCl ₄	283.1	45.0	C ₅ H ₁₂ , <i>n</i> -pentane	198.0	33.0
CCl ₂ F — CCIF ₂	214.1	33.7	C ₆ H ₅ Cl, chlorobenzene	359.1	44.6
CCIF ₃	28.8	40.3	C ₆ H ₆ , benzene	288.5	47.9
CO	−138.7	34.6	C ₆ H ₁₂ , cyclohexane	281.0	39.8
CO ₂	31.0	73.0	C ₆ H ₁₄ , <i>n</i> -hexane	234.8	29.5
COCl ₂	182	56	C ₆ H ₅ CH ₃ , toluene	320.6	41.6
CS ₂	273.0	72.9	C ₇ H ₁₆ , <i>n</i> -heptane	267.0	27.0
CHCl ₃	260.9	54.5	C ₈ H ₁₈ , <i>n</i> -octane	296.2	25.2
CH ₄ , methane	−82.2	45.8	Air	−140.9	37.2
CH ₃ OH, metha- nol	240.0	78.7			

9. VALUES OF γ FOR τ FROM 1 TO 35
(a) Values for τ from 1 to 3.5

$\tau \backslash \pi$	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	2.0	2.2	2.4	2.7	3.0	3.5
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	0.612	0.735	0.814	0.870	0.906	0.926	0.948	0.956	0.964	0.976	0.990	1.000	1.000	1.010	1.014
2	0.385	0.560	0.668	0.760	0.824	0.822	0.898	0.914	0.930	0.956	0.980	1.000	1.012	1.020	1.028
3	0.288	0.435	0.560	0.668	0.748	0.806	0.854	0.880	0.902	0.940	0.974	1.000	1.020	1.032	1.046
4	0.248	0.370	0.494	0.602	0.690	0.764	0.824	0.858	0.882	0.930	0.972	1.000	1.030	1.048	1.062
5	0.226	0.338	0.464	0.566	0.654	0.736	0.802	0.842	0.866	0.922	0.972	1.008	1.042	1.062	1.080
6	0.210	0.318	0.442	0.544	0.634	0.720	0.788	0.834	0.860	0.920	0.978	1.014	1.052	1.074	1.098
7	0.202	0.310	0.430	0.532	0.626	0.710	0.780	0.832	0.860	0.926	0.988	1.026	1.068	1.092	1.112
8	0.200	0.308	0.428	0.528	0.624	0.712	0.784	0.834	0.868	0.934	1.000	1.040	1.086	1.110	1.136
9	0.200	0.310	0.430	0.532	0.630	0.720	0.792	0.840	0.878	0.948	1.014	1.058	1.106	1.130	1.158
10	0.202	0.312	0.434	0.542	0.640	0.730	0.806	0.852	0.890	0.964	1.034	1.076	1.128	1.153	1.180
11	—	—	0.460	0.552	0.654	0.746	0.810	0.866	0.908	0.982	1.054	1.100	1.152	1.174	1.204
12	—	—	0.474	0.566	0.668	0.760	0.834	0.884	0.928	1.008	1.078	1.126	1.174	1.198	1.226
13	—	—	0.490	0.582	0.686	0.778	0.852	0.906	0.952	1.014	1.106	1.152	1.202	1.222	1.250
14	—	—	0.510	0.598	0.706	0.798	0.874	0.930	0.978	1.066	1.134	1.180	1.228	1.248	1.280
15	—	—	0.532	0.620	0.728	0.826	0.902	0.958	1.006	1.100	1.166	1.214	1.256	1.280	1.310
16	—	—	0.554	0.646	0.758	0.854	0.934	0.996	1.036	1.114	1.198	1.240	1.290	1.310	1.340
17	—	—	0.554	0.672	0.786	0.890	0.970	1.026	1.072	1.172	1.230	1.274	1.322	1.342	1.368
18	—	—	0.578	0.706	0.824	0.930	1.006	1.066	1.110	1.208	1.270	1.310	1.354	1.374	1.402
19	—	—	0.604	0.738	0.860	0.970	1.050	1.106	1.150	1.248	1.308	1.348	1.392	1.414	1.434
20	—	—	0.628	0.768	0.894	1.006	1.088	1.142	1.180	1.288	1.340	1.386	1.432	1.442	1.468
21	—	—	—	—	—	—	—	—	—	1.328	1.406	1.418	1.472	1.476	1.504
22	—	—	—	—	—	—	—	—	—	1.366	1.426	1.466	1.514	1.522	1.534

(b) Values for τ from 3.5 to 35

<div>τ π</div>	3.5	5	6	7	8	9	10	12	15	16	18	20	22	25	30	35
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
5	1.080	1.076	1.071	1.063	1.056	1.057	1.048	1.043	1.038	1.036	1.030	1.028	1.024	1.019	1.015	1.012
10	1.180	1.167	1.152	1.135	1.120	1.117	1.102	1.088	1.072	1.070	1.061	1.052	1.048	1.039	1.031	1.028
15	1.310	1.274	1.244	1.214	1.194	1.181	1.160	1.136	1.110	1.108	1.087	1.080	1.072	1.058	1.045	1.042
20	1.468	1.402	1.346	1.302	1.274	1.248	1.210	1.182	1.152	1.148	1.127	1.110	1.100	1.082	1.060	1.054
25	—	1.540	1.450	1.398	1.356	1.318	1.284	1.434	1.192	1.188	1.158	1.142	1.128	1.106	1.084	1.070
30	—	1.686	1.570	1.502	1.444	1.392	1.352	1.292	1.234	1.228	1.192	1.176	1.156	1.130	1.106	1.086
35	—	1.868	1.708	1.612	1.534	1.470	1.424	1.350	1.284	1.270	1.228	1.208	1.184	1.160	1.126	1.104
40	—	2.028	1.854	1.728	1.630	1.554	1.492	1.410	1.328	1.312	1.266	1.240	1.212	1.178	1.146	1.118
45	—	2.228	2.018	1.850	1.736	1.644	1.570	1.470	1.380	1.354	1.306	1.274	1.242	1.202	1.168	1.134
50	—	2.450	2.190	1.986	1.850	1.744	1.654	1.534	1.432	1.400	1.346	1.308	1.272	1.228	1.188	1.152
55	—	2.694	2.372	2.126	1.968	1.844	1.740	1.598	1.486	1.448	1.388	1.342	1.302	1.252	1.208	1.168
60	—	2.966	2.570	2.274	2.098	1.952	1.828	1.664	1.546	1.500	1.432	1.380	1.334	1.278	1.230	1.182
65	—	—	—	—	—	—	—	—	1.602	1.552	1.476	1.416	1.368	1.306	1.252	1.196
70	—	—	—	—	—	—	—	—	1.662	1.608	1.526	1.454	1.380	1.332	1.272	1.214
75	—	—	—	—	—	—	—	—	1.728	1.668	1.590	1.494	1.438	1.362	1.292	1.238
80	—	—	—	—	—	—	—	—	1.794	1.728	1.622	1.538	1.472	1.390	1.314	1.248
85	—	—	—	—	—	—	—	—	1.862	1.790	1.672	1.582	1.512	1.426	1.338	1.268
90	—	—	—	—	—	—	—	—	1.930	1.862	1.726	1.626	1.548	1.456	1.360	1.288
95	—	—	—	—	—	—	—	—	2.002	1.912	1.774	1.668	1.590	1.490	1.380	1.308
100	—	—	—	—	—	—	—	—	2.070	1.978	1.828	1.712	1.628	1.528	1.402	1.328

10. CONSTANTS OF EQ. (9.21)

<i>T</i>	<i>M</i> ₀	<i>M</i> ₁ × 10 ⁻³	<i>M</i> ₂ × 10 ⁻⁶	<i>M</i> ₋₃ × 10 ³	<i>T</i>	<i>M</i> ₀	<i>M</i> ₁ × 10 ⁻³	<i>M</i> ₂ × 10 ⁻⁶	<i>M</i> ₋₃ × 10 ³
300	0.000	0.0000	0.0000	0.0000	1700	0.9162	0.5780	0.4424	0.3824
400	0.0392	0.0130	0.0043	0.0364	1800	0.9635	0.6265	0.5005	0.3915
500	0.1133	0.0407	0.0149	0.0916	1900	1.009	0.6752	0.5619	0.3998
600	0.1962	0.0759	0.0303	0.1423	2000	1.0525	0.7240	0.6265	0.4072
700	0.2794	0.1153	0.0498	0.1853	2100	1.094	0.7730	0.6948	0.4140
800	0.3597	0.1574	0.0733	0.2213	2200	1.134	0.8220	0.7662	0.4203
900	0.4361	0.2012	0.1004	0.2521	2300	1.173	0.8711	0.8411	0.4260
1000	0.5088	0.2463	0.1134	0.2783	2400	1.210	0.9203	0.9192	0.4314
1100	0.5765	0.2922	0.1652	0.2988	2500	1.246	0.9696	1.0008	0.4363
1200	0.6410	0.3389	0.2029	0.3176	2600	1.280	1.0189	1.0856	0.4408
1300	0.7019	0.3860	0.2440	0.3340	2700	1.314	1.0683	1.1738	0.44505
1400	0.7595	0.4336	0.2886	0.34835	2800	1.346	1.1177	1.2654	0.4490
1500	0.8141	0.4814	0.3362	0.3610	2900	1.3775	1.1672	1.3603	0.4527
1600	0.8665	0.5296	0.3877	0.3723	3000	1.408	1.2166	1.4585	0.4562

11. VALUES OF $-\frac{G^\circ-H^\circ_0}{T}$ AND ΔH°_0
FOR GRAPHITE AND SELECTED GASES

Substance	$-(G^\circ-H^\circ_0)/T$ at <i>T</i> =							ΔH°_0 , kcal/mol
	298.16	400	600	800	1000	1200	1500	
C	0.5172	0.824	1.477	2.138	2.771	3.365	4.181	0
CO	40.350	42.393	45.222	47.254	48.860	50.194	51.864	−27.202
CO ₂	43.555	45.828	49.238	51.895	54.109	56.019	58.481	−93.969
COS	47.39	49.81	53.50	55.37	58.75	60.79	63.40	−22.2
CS ₂	48.28	50.90	54.89	57.97	60.51	62.57	65.44	−3.6
Cl ₂	45.951	48.148	51.297	53.614	55.453	56.979	0	0
HCl	37.734	39.771	42.588	44.597	46.171	47.472	49.096	−21.984
H ₂	24.423	26.422	29.203	31.186	32.738	34.010	35.590	0
H ₂ O	37.165	39.505	42.766	45.128	47.010	48.593	50.598	−57.107
H ₂ S	41.17	43.52	46.85	49.31	51.29	52.99	55.16	−19.53
NH ₃	37.958	40.362	43.822	46.461	48.659	50.574	53.086	—
N ₂	38.817	40.861	43.688	45.711	47.306	48.629	50.284	0
NO	42.980	45.134	48.090	50.202	51.864	53.245	54.964	21.477
NO ₂	49.14	51.58	55.13	57.83	60.05	61.96	64.38	—
O ₂	42.061	44.112	46.968	49.044	50.697	52.077	53.808	0
SO ₂	50.84	53.38	57.11	59.96	62.30	64.30	66.84	−85.746
SO ₃	51.87	54.74	59.26	62.94	66.08	68.83	72.40	−108.49
S ₂	47.33	49.47	52.52	54.78	56.57	58.06	59.92	—
CH ₄ , methane	36.46	38.86	42.39	45.21	47.65	49.86	52.84	−15.987
C ₂ H ₂ , acetylene	39.98	42.45	46.31	49.40	52.01	54.28	52.23	54.329
C ₂ H ₄ , ethylene	43.98	46.61	50.70	54.19	57.29	60.12	64.94	14.522
C ₂ H ₆ , ethane	45.27	48.24	53.08	57.29	61.11	64.63	69.46	−16.517

(concluded)

Substance	$-(G^\circ - H_0^\circ)/T$ at $T =$							ΔH_0° , kcal/mol
	298.16	400	600	800	1000	1200	1500	
CH_2CCH_2 , pro- padiene . . .	48.18	51.35	56.55	61.00	64.94	68.50	73.29	47.70
CH_2CHCH_3 , propylene . .	52.95	56.39	62.05	67.04	71.57	75.73	81.43	8.468
C_3H_8 , propane	52.73	56.48	62.93	68.74	74.10	79.07	85.86	—19.482
$\text{CH}_2\text{CHCHCH}_2$, 1,2-butadiene	57.11	61.21	68.10	74.11	79.52	84.47	91.18	42.00
C_4H_8 , 1-butene	59.25	63.64	71.14	72.82	83.93	89.55	97.27	4.96
C_4H_8 , isobutene	56.47	60.90	68.42	75.15	81.29	86.94	94.66	0.98
C_4H_8 , <i>cis</i> -2-bu- tene	58.67	62.89	69.94	76.30	82.17	87.62	95.12	3.48
C_4H_8 , <i>trans</i> -2- butene	56.80	61.31	68.84	75.53	81.62	87.22	94.91	2.24
C_4H_{10} , <i>n</i> -butane	58.54	63.51	72.01	79.63	86.60	93.08	101.95	—23.67
C_4H_{10} , isobutane	56.08	60.72	68.95	76.45	83.38	89.80	98.64	—25.30
C_5H_{12} , <i>n</i> -pen- tane	64.52	70.57	80.96	90.31	93.87	106.83	117.72	—27.23
C_5H_{12} , isopen- tane	64.36	70.07	80.12	89.44	97.96	105.87	116.78	—28.81
C_5H_{12} , neopen- tane	56.36	61.93	71.96	81.27	89.90	97.92	108.91	—31.30
C_6H_6 , benzene	52.93	56.69	63.70	70.34	76.57	82.40	90.45	24.00
C_6H_{14} , <i>n</i> -hexane	70.62	77.75	90.06	101.14	111.31	120.74	133.64	—30.91
CH_3NO_2	55.39	58.59	63.79	68.23	72.16	75.73	80.53	—14.55
$\text{C}_2\text{H}_5\text{OH}$	54.27	58.11	64.43	69.84	74.65	79.02	84.92	—52.26

12. RELATIONSHIPS BETWEEN VARIOUS ENERGY UNITS

Energy unit	erg	cal (15 °C)	l-atm (phys.)	cm ³ ·atm (phys.)
erg	1	$2.390\ 05 \times 10^{-8}$	$9.868\ 96 \times 10^{-10}$	$9.869\ 24 \times 10^{-7}$
cal (15 °C)	$4.184\ 01 \times 10^7$	1	$4.129\ 18 \times 10^{-2}$	$4.129\ 30 \times 10$
l-atm (phys.)	$1.013\ 28 \times 10^9$	$2.421\ 79 \times 10$	1	$4.000\ 03 \times 10^3$
cm ³ ·atm (phys.)	$1.013\ 25 \times 10^6$	$2.421\ 72 \times 10^{-2}$	$9.999\ 71 \times 10^{-4}$	1
kWh (abs.)	3.6000×10^{13}	$8.604\ 2 \times 10^5$	$3.552\ 82 \times 10^4$	$3.552\ 93 \times 10^7$

Note. 1 erg = 10⁻⁷ J.

13. FACTORS FOR CONVERTING SELECTED UNITS TO SI UNITS

$$1 \text{ l (dm}^3\text{)} = 1.0000 \times 10^{-3} \text{ m}^3$$

$$1 \text{ ml (cm}^3\text{)} = 1.0000 \times 10^{-6} \text{ m}^3$$

$$1 \text{ g/cm}^3 = 1000 \text{ kg/m}^3$$

$$1 \text{ g/ml (kg/l)} = 1000 \text{ kg/m}^3$$

$$1 \text{ cm}^3/\text{g} = 10^{-3} \text{ m}^3/\text{kg}$$

$$1 \text{ ml/g} = 1.0000 \times 10^{-3} \text{ m}^3/\text{kg}$$

$$1 \text{ l/mol (dm}^3\text{/mol)} = 1.0000 \times 10^{-3} \text{ m}^3/\text{mol}$$

$$t \text{ (}^\circ\text{C)} = T \text{ (K)} - 273.15$$

$$1 \text{ kgf} = 9.806\,65 \text{ N [1 N = (1 kg) \cdot (1 m):(1 s}^2\text{)]}$$

$$1 \text{ dyne} = 10^{-5} \text{ N}$$

$$1 \text{ at (techn)} = 98\,066.5 \text{ N/m}^2$$

$$1 \text{ atm (phys.)} = 101\,325 \text{ N/m}^2$$

$$1 \text{ kg} \cdot \text{m} = 9.806\,65 \text{ J [1 J = (1 N) \cdot (1 m)]}$$

$$1 \text{ l} \cdot \text{atm} = 101.328 \text{ J}$$

$$1 \text{ cal} = 4.1868 \text{ J}$$

$$1 \text{ cal/mol} \cdot \text{K} = 4.1868 \text{ J/mol} \cdot \text{K}$$

14. COMMON LOGARITHMS (FOUR-PLACE)

Number	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	11	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5052	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	11
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	12
35	5441	5453	5465	5478	5490	5502	5515	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

(continued)

Number	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4

(concluded)

Number	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9764	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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